



HAL
open science

Different Approaches to Mid-Valent, Paramagnetic Half-Sandwich Complexes of the Heavier Group 6 Metals

Rinaldo Poli

► **To cite this version:**

Rinaldo Poli. Different Approaches to Mid-Valent, Paramagnetic Half-Sandwich Complexes of the Heavier Group 6 Metals. SYNLETT, 1999, 1999 (7), pp.1019-1028. 10.1055/s-1999-2746 . hal-03309810

HAL Id: hal-03309810

<https://hal.science/hal-03309810>

Submitted on 4 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Different Approaches to Mid-Valent, Paramagnetic Half-Sandwich

Complexes of the Heavier Group 6 Metals

Rinaldo Poli

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté des Sciences
"Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, 21 100 Dijon, France

Fax (+33) 380386098; E-mail: poli@u-bourgogne.fr

Received 26 January 1999

Abstract: The synthesis of deceptively simple carbonyl-free, mid-valent half-sandwich Mo and W compounds containing mainly phosphine, halide, and hydride ligands actually involves a number of complications requiring several tricks or synthetic detours to be overcome. The stability of some of the target systems also necessitates particular synthetic conditions.

- 1 Introduction
- 2 A Metathetical Route to CpMo(III) Complexes
- 3 A Reductive Route to CpMo(III) Complexes
- 4 Further Reduction to Noncarbonyl Mo(II) Derivatives
- 5 Paramagnetic hydride derivatives of Mo(III), Mo(V), and W(V)

Keywords: molybdenum, tungsten, cyclopentadienyl complexes, phosphine complexes, paramagnetic complexes

1 Introduction

Over a number of years, interest in my laboratory has been attracted by paramagnetic organometallic complexes, a class of compounds that has developed at a slower pace relative to the diamagnetic counterparts. Two reasons for this state of affairs are the relevance of the EAN rule in organometallic chemistry, dictating a greater stability for electronically saturated, diamagnetic configurations, and the greater difficulty associated with the handling and characterization of paramagnetic compounds. The reasons, on the other hand, to be interested in compounds of this type are the potential for discovering interesting ground state properties and, indeed, the expected greater reactivity, which could lead to interesting new stoichiometric and catalytic transformations.

Early work on organometallic, mostly low-valent, carbonyl-based, radical species had shown a higher lability of the metal-ligand bonds relative to saturated counterparts. However, these low-valent species are most often unstable, limiting their study and utility. We considered that the EAN rule loses importance as the oxidation states is raised, paralleling a weakening of the metal-ligand back-bonding interaction to typical organic substrates (without necessarily reducing their activation). These considerations led to our interest in mid-valent, paramagnetic organometallic compounds, where one could hope to combine an increased stabilization of the odd-electron configuration with substrate activation and lability with respect to a variety of fundamental reactions. In addition, we have chosen to work with half-sandwich compounds,

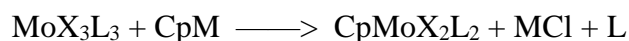
since the cyclopentadienyl ligand forms stable and inert bonds with transition metals, imparting solubility in most common organic solvents. At the same time, coordination by a single cyclopentadienyl ligand, rather than two or three, leaves a sufficient number of other coordination positions available for coordination and activation of potential substrates and reagents for the investigation of chemical reactivity. Most of our studies have been carried out with group 6 metals, especially molybdenum, given the involvement of these metals in a variety of catalytic processes such as polymerization, hydrodesulfurization, and dinitrogen reduction, and the availability of several oxidation states and electronic configurations for these metals.

Our studies have indeed allowed us to contribute to a better understanding of fundamental questions, such as how a spin state change may affect thermodynamic stabilization, reactions rates, and structural changes in open-shell organometallic chemistry.¹ We have also discovered new reaction pathways, such as an electron transfer-catalyzed ligand substitution where, for the

first time in organometallic chemistry, the order of reactivity is reversed (faster for even- than for odd-electron configurations). These developments are analyzed in other recent review articles.¹⁻³ In the spirit of this Journal, I shall focus on the synthetic aspects of our research in the present account.

2 A Metathetical Route to CpMo(III) Complexes

We have long been (and still are) interested in developing the chemistry of the 17-electron CpMoX₂L₂ system. Initial studies were focused on complexes with L = tertiary phosphine, a few examples of which had been previously described briefly by the Green group.⁴ The first synthetic approach to these materials consisted in the introduction of the cyclopentadienyl ring on a coordination compound of Mo(HI) by a metathesis process (eq. 1). The first try immediately gave the desired result, namely the synthesis of CpMoX₂(PMe₃)₂ (X = Cl, Br or I) from the corresponding MoX₃(PMe₃)₃ and TICp in THF or toluene.⁵



Equation 1

The Mo(III) precursors are available from the corresponding tetrahydrofuran complexes, MoX₃(THF)₃. The trichloro complex has long been known and is available in three easy steps from MoCl₅,⁶ the last one involving separation of the insoluble (in THF) product from the excess tin reagent by extraction into CH₂Cl₂ and filtration. During our work, we realized that MoCl₃(THF)₃ converts relatively rapidly to the dinuclear metal-metal bonded Mo₂Cl₆(THF)₃ on standing in CH₂Cl₂,⁷ a process that had in fact been previously described by Boyd and Wedd on the basis of an optical study.⁸ Our investigation, which was based on a ¹H NMR monitoring, gave additional insights, including the identification of the Mo₂Cl₆(THF)₄ intermediate. The contamination of MoCl₃(THF)₃ by varying amounts of dinuclear condensation products does not appear to affect most of the subsequent synthetic applications, but we have developed a slight modification of the synthetic procedure whereby the MoCl₃(THF)₃ and Sn solids are separated mechanically by virtue of their different density, thereby avoiding the dichloromethane extraction.⁹ The corresponding tribromo and triiodo derivatives MoX₃(THF)₃ (X = Br, I) cannot be prepared similarly to the trichloro complex because higher valent MoX_n

precursors are nonexistent or not easily available, thus we developed alternative procedures consisting of the halogenation of lower-valent carbonyl precursors, suitable to large scale syntheses.¹⁰⁻¹²

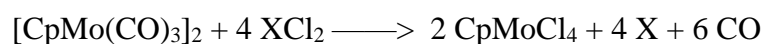
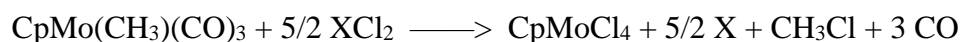
A problem with the synthesis of eq. 1 is the sacrifice of one mole of the phosphine ligand. Another problem is that phosphine ligands bulkier than PMe_3 do not cleanly afford the MoX_3L_3 precursor,⁹ limiting the applicability of this method. Finally, even the PMe_3 system afforded less than satisfactory results. The poisonous thallium reagent had to be used to avoid the reductive competitive processes that are prevalent with the sodium reagent. This, however, required forcing conditions for the completion of the metathesis process [several hours reflux in THF ($\text{X} = \text{Cl}, \text{Br}$) or toluene ($\text{X} = \text{I}$)]. While the desired 17-electron half-sandwich complex was the major product in each case, small amounts of reduced materials [$\text{MoX}_2(\text{PMe}_3)_4$ and $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$] were also obtained, especially for $\text{X} = \text{Cl}$.

Although this synthetic procedure was also found acceptable for the $\text{CpMoX}_2(\text{dppe})$ system,¹³ an alternative, more selective methodology which could also be of wider applicability was clearly needed. As shown in the next section, such a methodology was rapidly found. Several problems, however, were also encountered during that alternative procedure, as will be accounted in more detail later, leading us to occasionally reconsider a metathetical entry into CpMo(III) chemistry. Subsequent efforts in this area have involved the direct reactions of $\text{MoX}_3(\text{THF})_3$ with Cp delivering reagents (eq. 1, $\text{M} = \text{Na}, \text{Tl}, \text{Me}_3\text{Si}$) in order to access either CpMoCl_2 (which is a stable compound, *vide infra*) directly or an adduct containing a labile solvent molecule such as THF or MeCN. These trials have always ended in big disappointments. Attempts have also miserably failed to introduce the indenyl ring via either the sodium or thallium reagent: a few crystals of $[(\eta^5\text{-C}_9\text{H}_7)\text{MoI}_2]_2$ have been obtained¹⁴ and EPR signals consistent with the expected $(\eta^5\text{-C}_9\text{H}_7)\text{MoX}_2\text{L}_2$ have been observed for $\text{L}_2 = \text{dppe}$, but the reactions were dominated by the reductive pathway¹⁵ and by other complex ligand exchange pathways¹⁶ and clean products could never be isolated.

3 A Reductive Route to CpMo(III) Complexes

One often gets inspired from reading the literature, especially when the simplest, more logical avenues end up in unsatisfactory results or in total failures. The 17-electron complexes previously reported by Green had been made by ligand addition to $[(\eta^5\text{-C}_5\text{H}_4\text{Pr}^i)\text{Mo}(\mu\text{-Cl})_2]_2$,⁴ which was made by HCl addition to an unusual reagent, $(\eta^6\text{-C}_6\text{H}_5)(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CMe}_2)\text{Mo}$, this in turn being available from a metal vapor synthetic procedure. We were not equipped to carry

out metal vapor reactions, but the existence of the trachloro-bridged species led us to believe that the corresponding unsubstituted Cp analogue could also be made and that this could easily form adducts with a variety of ligands. Shortly prior to our impasse, Green and Mountford had communicated that the reduction of $(C_5H_4R)WCl_4$ ($R = Me, Pr^i$) affords the dinuclear W(III) system, $[(C_5H_4R)WCl_2]_2$,¹⁷ leaving hope that an analogous reductive procedure could work also for Mo. The needed precursor $CpMoCl_4$ was a known compound,¹⁸ available by reaction of HCl in Et_2O with any of a number of oxo or oxochloro derivatives, but described as a highly hygroscopic species. On the other hand, Schrock had previously reported a high yield synthesis of Cp^*MCl_4 ($M = Mo, W$)¹⁹ by PCl_5 oxidation of easily available $Cp^*M(CH_3)(CO)_3$. Contemporarily with the Green group,²⁰ we were pleased to find out that Schrock's method could conveniently be adapted to the synthesis of $CpMoCl_4$ from $CpMo(CH_3)(CO)_3$ and PCl_5 (eq 2, $X = PCl_3$).¹³ The Green contribution²⁰ also showed the formation of a tetrabromo analogue, $(C_5H_4Me)MoBr_4$, by Br_2 oxidation of the tricarbonyl dimer $[(C_5H_4Me)Mo(CO)_3]_2$. We found that the tetrachloro species are equally available from the tricarbonyl dimers precursors (eq 3, $X = PCl_3$), the latter providing the notable advantage of being more easily synthesized than the tricarbonylmethyl reagent of equation 2. The unsubstituted Cp complex is even available from a number of commercial sources. We subsequently further simplified the synthetic procedure by using $PhICl_2$ as the oxidizing agent (eq. 3, $X = PhI$)²¹ and extended it to the Cp^* system.²² The $PhICl_2$ reagent is easily available from PhI and Cl_2 ²³ and has the advantage over PCl_5 of not being sensitive toward moisture, thus it can be handled in air (though it must be kept in the dark in a refrigerator if long term storage is needed).

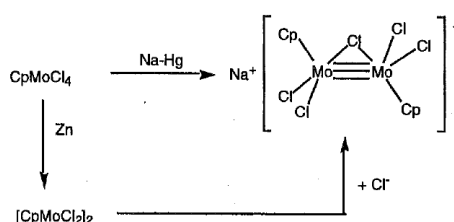


Equation 2 and 3

Once the $CpMoCl_4$ was at hand in reproducibly high yields, we considered its reduction to phosphine adducts of Mo(III). While communicating our foray into this area at various conferences, Tom Baker informed us of his synthesis of $Cp^*MoCl_2(PMe_3)_2$ and of the ortho-metallated $Cp^*WCpH(CH_2PMe_2)(PMe_3)$ complex by sodium reduction of $Cp^*MCl_4(PMe_3)$, reactions that were eventually published a few years later.²⁴ Eager to access the desired 17-

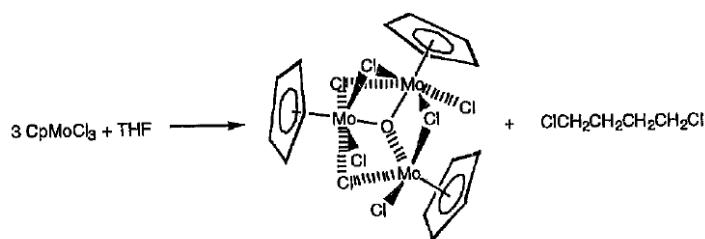
electron $\text{CpMoCl}_2\text{L}_2$ adducts in a one-pot synthesis from CpMoCl_4 , we preceded to add phosphine ligands to the Mo(V) precursor, with the intention of carrying out an *in situ* reduction of the resulting adducts. However, greed often leads to bitter punishment. We found out that the CpMoCl_4 -PR₃ combination leads to a complex reduction process, yielding MoCl_3L_3 , (with loss of the Cp ring !) and other uncharacterized products (rates in the order $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PMePh}_2$). On the other hand, the addition of basic phosphine ligands (even primary ones) to the more encumbered and less acidic Cp^*MoCl_4 or to tungsten analogues leads to stable adducts.^{19,25-28} The reduction of Lewis acidic metal halide reagents by basic phosphine ligands is a known nuisance, which we have encountered time and again in other areas, such as the coordination chemistry of iron²⁹⁻³⁰ and the organometallic chemistry of niobium.³¹

Thus, in order to circumvent the phosphine-induced CpMoCl_4 decomposition, we decided to first reduce the CpMoCl_4 material to CpMoCl_2 , then add the desired phosphine, in two separate steps. As it turns out, this reduction process has also reserved surprises for us, both good and bad. While, almost contemporarily with our studies, Green, Hubert and Mountford had no trouble obtaining $[(\text{C}_5\text{H}_4\text{R})\text{MoC}_2]_2$ by Na-Hg reduction of $(\text{C}_5\text{H}_4\text{R})\text{MoCl}_4$ ($\text{R} = \text{Me}, \text{Pr}^i$),²⁰ the corresponding reduction of the unsubstituted Cp derivative led to an ionic compound that turned out to be the sodium salt of $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^-$ (Scheme 1). This anion did not react cleanly with phosphine ligands, creating yet another obstacle between us and our target 17-electron system. The good news, however, is that this anion, subsequently prepared also by addition of Cl^- to CpMoCl_2 and structurally characterized as the $[\text{Ph}_3\text{PNPPH}_3]^+$ salt, revealed an unprecedented and fascinating structure featuring a Mo-Mo triple bond bridged by a single Cl^- ligand.³² Evidently, the sodium cations produced during the reduction process are unable to completely abstract chloride from the relatively unencumbered and acidic Cp-containing reduced Mo(III) complex. Later, the Green group showed that analogous anionic Cl^- adducts are also formed by the less acidic and more encumbered $[(\text{C}_5\text{H}_4\text{R})\text{MoCl}_2]_2$ compounds and by the W analogues.³³ On the basis of this Lewis acidity argument, we finally arrived at the successful use of Zn as the reducing agent (Scheme 1), affording the desired CpMoCl_2 in good yields.³⁴



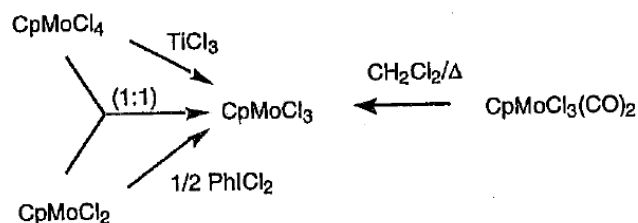
Scheme 1

The Zn^{2+} ion has a greater Lewis acidity than Na^+ and is able to fully abstract Cl^- , leaving behind the neutral CpMoCl_2 . Furthermore, the product separation is simplified since CpMoCl_2 is essentially insoluble in THF while ZnCl_2 forms the soluble $\text{ZnCl}_2(\text{THF})_2$ complex which can be readily washed away. Even this reduction procedure, however, is not completely fool-proof. The reaction initially produces the Mo(IV) intermediate CpMoCl_3 ,³⁵ which is rather thermally sensitive and is able to exchange chlorides with the oxygen atom of the THF solvent under mild conditions, affording $\text{Cp}_3\text{Mo}_3\text{Cl}_7\text{O}$ and 1,4-dichlorobutane (eq. 4).³⁶ The use of coarse Zn grains leads to slow reactions with extensive decomposition, while the use of a fine Zn powder at room temperature leads to strong exotherms, also resulting in decomposition. The best results (> 70% yield) are obtained by the use of a fine Zn powder and low temperatures (-20°C).



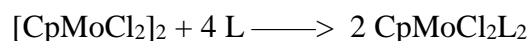
Equation 4

Incidentally, the CpMoCl_3 material had not been previously reported.³⁷ Since this can be imagined to be a potentially versatile reagent, we have invested some time in its synthesis, which turned out to be possible by the four different synthetic routes outlined in Scheme 2.^{35,38} It was particularly amusing to realize that the dicarbonyl precursors $\text{CpMoX}_3(\text{CO})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) had been known since 1966^{39,40} and had been described as sensitive compounds that readily lose CO in solution,³⁹ but no studies of the decarbonylation products had ensued. As it turns out, this is in fact the simplest synthesis of CpMoCl_3 ⁴¹ and is extendable also to the tribromide and triiodide analogues.³⁸



Scheme 2

Coming back to Mo(III) chemistry, the last step of the synthetic procedure, namely the addition of the phosphine ligand, proceeded as expected and allowed us to obtain a variety of bis-phosphine adducts (eq. 5).^{13,34,42,43} The corresponding dibromide and diiodide derivatives were subsequently obtained by relatively facile halide metathesis processes.^{34,44} The use of sodium salts in THF favored the quantitative conversion of the dichloro to the diiodo species, while soluble salts in dichloromethane strongly favored the opposite process. The exchange of the phosphine ligand is an even more facile reaction and proceeds by a dissociative mechanism. We have proposed that the 15-electron intermediate of this exchange process is energetically stabilized by a spin change.^{42,45} More recently, the addition reaction of eq. 5 has been extended to the high-yield synthesis of the butadiene complex $\text{CpMoCl}_2(\eta^4\text{-C}_4\text{H}_6)$,⁴⁶ previously available only in < 50% yields by a disproportionation procedure.⁴⁷ Other derivatives with diamine and with bifunctional ligands (phosphine-amine, phosphine-thioether, etc.) are also being prepared and characterized.^{48,49}



Equation 5

A few more words on the versatile CpMoCl_2 reagent are in order. Its structure is inferred as dinuclear with four bridging chloride ligands by analogy with the crystallographically characterized $[(\text{C}_5\text{H}_4\text{Pr}^i)\text{MoCl}_2]$ and $[(\text{C}_5\text{Me}_4\text{Et})\text{MoCl}_2]_2$ compounds.^{4,50} The bromo and iodo complexes $[\text{Cp}^*\text{MoX}_2]_2$ (X = Br, I) and $[(\eta^5\text{-C}_9\text{H}_7)\text{MoI}_2]_2$ also display an analogous structure.^{14,51-54} However, this compound is essentially insoluble in all common solvents, preventing its spectroscopic characterization in solution and *its purification*. One is stuck, unfortunately, with using the material as obtained from the synthetic procedure. In order to

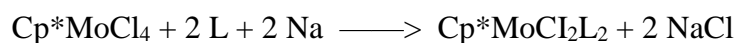
avoid unsatisfactory results in the follow-up reactivity studies (in which we have incurred time and again), it is thus absolutely essential that the synthesis be carried out with a slight defect of Zn and from absolutely pure CpMoCl₄. Furthermore, the CpMoCl₄ precursor is, itself, a sparingly soluble, difficult to purify, and extremely moisture sensitive compound. It, in turn, must be synthesized from absolutely pure starting materials. The use of crude [CpMo(CO)₃]₂, as obtained from the classical Manning procedure (Fe³⁺ oxidation of [CpMo(CO)₃]⁻),⁵⁵ has repeatedly led to inconsistent results and also to some occasional surprises, such as the incorporation of iron to yield the complex structure of [Cp*₂Mo₂(μ-I)₄][Cp*₂Mo₂(μ-I)₂(μ-O)][FeI₄].⁵⁶ A reliable procedure involves the purification of [CpMo(CO)₃]₂ by Soxhlet extraction with dichloromethane. Finally, the thorough washing of the ZnCl₂(THF)₂ by-product from CpMoCl₂ is absolutely essential. The direct addition of PMe₃ to the CpMoCl₂ suspension in the presence of ZnCl₂ led to the formation of a product which, on the basis of elemental analyses and EPR spectroscopy, is formulated as either the zwitterionic CpMo(PMe₃)₃(ClZnCl₃) or the isomeric [CpMoCl(PMe₃)₃]₂[Zn₂Cl₆].⁵⁷ Embarrassing confusions in the identity of crystallographically characterized complexes⁵⁸ can also be apparently attributed to Zn contamination of the cyclopentadienyl starting material.⁵⁹

Given the problems associated with the zinc reduction of CpMoCl₄, we have devoted additional attention to the direct, one-pot reductions of CpMoCl₄ by Na-Hg in the presence of the desired ligand. As stated above, this procedure is unsatisfactory with basic phosphines but other ligands that are not oxidized by CpMoCl₄ should be compatible with the reaction conditions. At the same time, their coordination at some stage of the reduction procedure should favor the complete removal of the chloride ions by Na⁺. The bifunctional ligand Ph₂PCH₂CH₂SMe satisfies all necessary requirements, the one-pot reduction of CpMoCl₄ in the presence of this ligand providing a good yield synthesis of CpMoCl₂(Ph₂SCH₂CH₂SMe).⁴⁹ The intermediate CpMoCl₄(MeSCH₂CH₂PPh₂) derivative may even be isolated as a pure product. Diene ligands do not allow a direct one-pot synthesis of CpMoCl₂(η⁴-diene) using sodium, because of the parasite anionic diene polymerization under these conditions. The use of zinc eliminates the competitive polymerization process, but the separation of the soluble zinc dichloride by-product from the diene-Mo(III) complex is problematic, thus the diene addition to isolated CpMoCl₂ remains more convenient.⁶⁰ A combined reduction-addition-metathesis process occurs in a single step to convert CpMoCl₄ to CpMo(η³-C₃H₅)₂ in good yields (eq. 6).⁶¹ This compound was previously available only from a 5-step procedure from MoCl₅ in unreported yields.⁶²



Equation 6

Cp^* analogues of the above systems are easier to synthesize. As mentioned above, $\text{Cp}^*\text{MoCl}_2(\text{PMe}_3)_2$ was prepared by Baker by one-pot reduction of Cp^*MoCl_4 in the presence of PMe_3 (eq. 7).²⁴ The same procedure also affords bis- PMe_2Ph and dppe analogues.^{63,64}

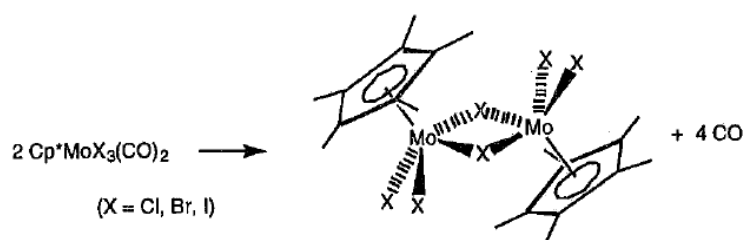


($\text{L} = \text{PMe}_3$, PMe_2Ph , or $\text{L}_2 = \text{dppe}$)

Equation 7

The use of Cp^* has advantages and disadvantages over the use of Cp . The direct, one-pot process of eq. 7 does not suffer from the competitive reductive process, and the Cp^* products are less air sensitive, more soluble, and easier to crystallize than the Cp analogues. On the other hand, the steric bulk of Cp^* does not allow the formation of derivatives with bulky L ligands. PMe_2Ph and dppe are the bulkiest ligands to give stable complexes of this family. The use of bulkier PMePh_2 and PPh_3 only leads to the formation of $[\text{Cp}^*\text{MoCl}_2]_2$.⁶³

As mentioned above, CpMoCl_3 was made in our laboratory for the first time. Its insolubility, however, prevented its structural characterization, although the magnetic moment suggests the presence of antiferromagnetic interactions in a dinuclear or oligonuclear structure without metal-metal bonds. Work on the more soluble Cp^* derivative, prepared by the decarbonylation procedure (eq. 8), has allowed to verify the dinuclear structure by X-ray crystallography.^{53,65}



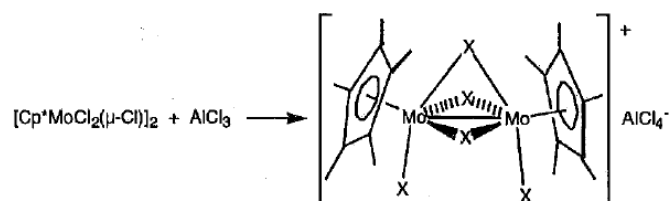
Equation 8

The solution behavior of the bromide and iodide derivatives, however, turned out more complex than expected, revealing equilibria with or irreversible transformations to more complex structures, for instance eq. 9 for the bromide and eq. 10 for the iodide. All these compounds exhibit rather complex and interesting redox behaviours.⁵³



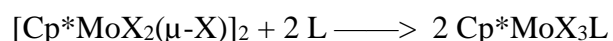
Equation 9 and 10

The chloride compound maintains the neutral dinuclear structure shown in eq. 8 under all conditions, but a chloride ligand abstraction with rearrangement to a Mo-Mo bonded structure is enforced by Lewis acids (eq. 11).⁶⁶



Equation 11

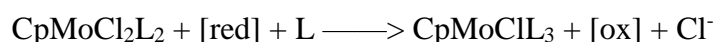
From a synthetic point of view, the chloride and bromide derivatives have been used to access a number of 16-electron ligand adducts of formula $\text{Cp}^*\text{MoX}_3\text{L}$ (eq. 12), including $[\text{Cp}^*\text{MoX}_4]^-$.²⁵



Equation 12

4 Further Reduction to Noncarbonyl Mo(II) Derivatives

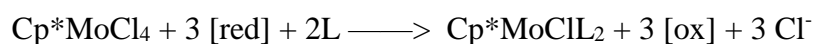
In order to open coordination sites and favor chemical reactivity, a high level of electron richness on the compound is helpful. The complete substitution of carbonyl ligands with phosphine donors should accomplish this goal, as illustrated for instance by the greater reactivity of Mo(PMe₃)₆ relative to Mo(PMe₃)_x(CO)_{5-x} in C-H bond activation processes.⁶⁷ Half-sandwich Mo(II) complexes of the CpMoXL₃ type frequently contain π acidic ligands (mostly L = CO, but also L = carbene, L₂ = diene or XL = allyl),⁶⁸⁻⁷⁰ or moderately acidic ligands such as phosphites.⁷¹ Fully phosphine-substituted examples were limited to X = H.⁶⁷ We wanted to access similar derivatives where X = π -donor ligand, with the idea of destabilizing a saturated structure by filled-filled repulsion and stabilizing the unsaturated one by π -donation,⁷² thereby favoring an open-shell configuration. Carbonyl-containing precursors of type CpMoXL₃ are abundant and easily accessible, and one could envisage a simple CO substitution process. Unfortunately, as is well known, the substitution of CO ligands is a facile process in CO-rich complexes but becomes progressively more difficult as the number of CO ligand decreases, the last CO being almost impossible to remove, especially in electron-rich systems. Work by Lapinte has shown that CO substitution by phosphine or phosphite on Cp*MoH(CO)₃ or [CpMo(CO)₃(PR₃)]⁺/LiAlH₄ stopped at the monocarbonyl level.⁷³ Thus, the easily available CpMoX(CO)₃ compounds are not suitable precursors to fully phosphine-substituted CpMoXL₃. This left us with the use of a reductive route on the CpMo(III) compounds that we had just synthesized (see previous section) according to eq. 13.



Equation 13

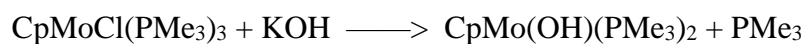
The reaction works as expected for L = PMe₃ and PMe₂Ph and [red] = Na amalgam,^{57,74} with one caveat. Once again, one must not be too greedy and take a shortcut with a one-pot reduction of CpMoCl₂ in the presence of three equivalents of L. The addition of three equivalents of L to CpMoCl₂ in THF (the solvent required for the Na reduction) yields a large amount of precipitate that is no longer able to engage in a clean reduction step. Subsequent investigations⁴⁵ have shown that this precipitate is [CpMoCl(PMe₃)₃]⁺Cl⁻. Good results, however, are obtained by adding two equivalents of L to CpMoCl₂, allowing the formation of CpMoCl₂L₂ to go to completion, then add the third equivalent of L and the reducing agent at the same time.

The study of compounds CpMoClL₃ revealed a steric effect controlling the access to the desired open-shell systems: upon warming, CpMoCl(PMe₂Ph)₃ establishes an equilibrium with the 16-electron and *paramagnetic* bis-phosphine analogue, CpMoCl(PMe₂Ph)₂, whereas the less encumbered PMe₃ system does not engage in a phosphine dissociation process. This open-shell product eluded isolation. On the other hand, the more encumbered Cp* system allowed the synthesis and isolation of Cp*MoClL₂ (L = PMe₃, PMe₂Ph or L₂ dppe), the first 16-electron half-sandwich Mo(II) derivatives with a spin triplet ground state.⁷⁴ No particular complication was experienced in the synthesis of these compounds directly from Cp*MoCl₄ (eq. 14), besides the fact that the PMe₃ derivative requires the use of an argon atmosphere and the use of strictly two equivalents of PMe₃. Under dinitrogen, the N₂ adduct is obtained as previously reported by Baker,²⁴ whereas the use of three equivalents of the phosphine affords sterically encumbered Cp*MoCl(PMe₃)₃.⁵⁷ An equilibrium process between this product and the bis-phosphine analogue is very slow.⁷⁵ A kinetic, thermodynamic, and computational study of the CO and N₂ addition to Cp*MoCl(PMe₃)₂ has allowed us to gain a considerable insight into the effect of a spin state change on reaction rates for organometallic ligand addition processes.⁷⁶



Equation 14

One of our goals was therefore achieved: the use of electron donating ligands (phosphines) and a π donor ligand (chloride) favors ligand dissociation and stabilizes an open-shell configuration. No particularly interesting chemical reactivity such as C-H activation, however, is displayed by these unsaturated Mo(II) complexes. It is relevant to note here that the reduction of Cp*WCl₄/PMe₃ was reported to afford the C-H oxidative addition product Cp*W(CH₂PMe₂)(PMe₃)(H)Cl,²⁴ presumably via a Cp*WCl(PMe₃)₂ intermediate which is more reactive than our Mo analogue. It is also known that unsaturated (η^5 -C₅H₄R)MoHL₂ intermediates (generated by photoinduced H₂ elimination from the stable trihydrides) catalyze H/D exchange reactions between C₆D₆ and other substrates.⁴ It was therefore desirable to generate other CpMoXL₂ compounds in order to understand the influence of X on the stability and reactivity of the unsaturated complex. The hydroxide system, obtained by the metathesis reaction 15, has given us unexpectedly interesting results.^{77,78}



Equation 15

The first peculiar observation is the stability of the open-shell structure, even in the presence of PMe_3 , contrasting with the preference of the chloride system for the saturated tris-phosphine system, although OH is less bulky than Cl. This stabilization is related to the greater π donating ability of OH, as confirmed by computational studies. A second point of interest is the ability of this compound to undergo H/D exchange in C_6D_6 at the PMe_3 positions. Most notably, a diversion of the OH π -donating lone pairs into H-bonding with the protic solvent, thereby rendering the metal less saturated and more reactive.⁷⁸ The $\text{CpMo(OH)(PMe}_3)_2$ compound is exceedingly soluble in pentane and cannot be crystallized from concentrated solutions at -80°C . By comparison, the $\text{CpMoCl(PMe}_3)_3$ precursor is easily crystallized under the same conditions. This solubility enhancement is consistent with a negligible Mo-OH bond polarity and absence of self-association via H-bonding, both resulting from the strong HO-Mo π donation. The next synthetic challenge is to generate less soluble versions of the hydroxo system as well as other compounds of this class where a control of the extent of π donation from X is possible.

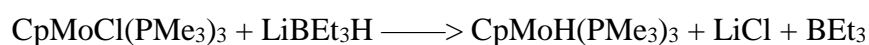
5 Paramagnetic hydride derivatives of Mo(III), Mo(V), and W(V)

Since the hydride ligand is involved in a variety of stoichiometric and catalytic processes, it was of interest to generate paramagnetic versions of known hydride complexes and to probe their reactivity. A particular interest consisted in the achievement of the elementary process of H_2 reductive elimination from a paramagnetic polyhydride system. This process has the potential of generating highly unsaturated, 15-electron species, analogous to the 16-electron species obtained by H_2 reductive elimination from a saturated dihydride complex.

Although reductive elimination of an alkane from a saturated dialkyl complex is known to be accelerated by oxidation to a radical system, the reductive elimination of H_2 from an oxidized polyhydride system had never been reported. The reason for this is probably the greater propensity of paramagnetic hydrides to undergo other decomposition processes, namely deprotonation⁷⁹ and disproportionation.⁸⁰ A large body of work suggests that both of the latter two pathways may be discouraged by employing a sterically protecting coordination sphere. A

large ligand bulk would in fact lower the kinetic acidity, thereby slowing down proton transfer to an acceptor base (the rate determining step of the deprotonation mechanism) and at the same time lower the ability of a donor solvent molecule to coordinate the metal center, which seems a prerequisite for the rate determining electron transfer step of the disproportionation pathway. The generation of paramagnetic hydride complexes by oxidation requires the availability of the saturated diamagnetic precursors. Thus, our work started with the synthesis of stable 18-electron hydride complexes.

Group 6 metal complexes of stoichiometry $(\eta^5\text{-C}_5\text{R}_5)\text{MHL}_3$ and $(\eta^5\text{-C}_5\text{R}_5)\text{MH}_3\text{L}_2$ ($\text{M} = \text{Mo}, \text{W}$) allow a good control of the steric and electronic properties via the choice of the cyclopentadienyl and phosphine substituents. $\text{CpMoH}(\text{PMe}_3)_3$ was first reported by Brookhart *et al.*⁶⁷ as an uncrystallizable wax, impure from cyclopentadiene oligomers, obtained from the oxidative addition of CpH to $\text{Mo}(\text{PMe}_3)_6$. We have generated this compound from $\text{CpMoCl}(\text{PMe}_3)_3$ and LiBEt_3H , eq. 16, therefore in the absence of nonvolatile organic contaminants, without improving the crystallinity of the compound.

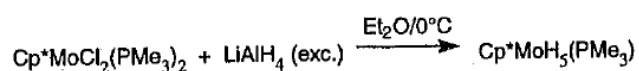


Equation 16

Every subsequent reactivity study has therefore required the generation of the hydride compound *in situ* from the chloride precursor. This nuisance did not prevent us from developing interesting oxidation chemistry,^{81,82} but it demanded the completion of the metathesis step to avoid complications during the subsequent transformations. For instance, oxidation of this product in a wet organic solvent engages water as both a ligand and a proton source (but not as a base!) to afford the Mo(III)-hydroxo complex $[\text{CpMo}(\text{OH})(\text{PMe}_3)_3]^+$, amongst other products. Occasionally, the use of a hydride source that was contaminated by unconverted chloride precursor afforded crystals that turned out to contain a solid solution of $[\text{CpMo}(\text{OH})(\text{PMe}_3)_3]^+$ and $[\text{CpMoCl}(\text{PMe}_3)_3]^+$ tetrafluoroborate.⁸² The oxidation in dry solvents has allowed the formation of the relatively stable Mo(III) hydride complex $[\text{CpMoH}(\text{PMe}_3)_3]^+$. This eventually decomposes by *both* deprotonation and disproportionation pathways. A kinetic study has allowed (for the first time) a quantitative assessment of both pathways for the same system.⁸¹ The steric protection in this system has also allowed, for the first time, the isolation and X-ray

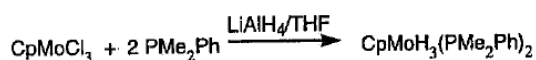
study of the intermediate of the disproportionation pathway, $[\text{CpMoH}(\text{PMe}_3)_3\text{-(MeCN)}][\text{BF}_4]_2$.⁸¹ An even more stable Mo(III) hydride compound could be envisaged starting from $\text{Cp}^*\text{MoH}(\text{PMe}_3)_3$. Unfortunately, the synthesis of this product according to the protocol of eq. 16 from $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_3$ affords a mixture of $\text{Cp}^*\text{MoH}(\text{PMe}_3)_3$ and $\text{Cp}^*\text{MoH}_3(\text{PMe}_3)_2$,⁵⁷ thus the generation of $[\text{Cp}^*\text{MoH}(\text{PMe}_3)_3]^+$ must await a more selective synthesis of the neutral precursor.

Compounds of the $(\eta^5\text{-C}_5\text{R}_5)\text{MH}_3\text{L}_2$ family are known for both Mo and W. The Mo complexes were reported from the reaction of a variety of hydride sources with the corresponding $(\text{Ring})\text{MoCl}_3\text{L}_2$ (Ring = Cp; $\text{L}_2 = \text{dppe}$)⁸³ or $(\text{Ring})\text{MoCl}_2\text{L}_2$ (Ring = $\text{C}_5\text{H}_4\text{Pr}^i$; $\text{L} = \text{PMe}_3$, PMe_2Ph or $\text{L}_2 = \text{Pr}^i_2\text{PCH}_2\text{CH}_2\text{PPr}^i_2$).⁴ Since we had at our disposal a number of new $(\text{Ring})\text{MoCl}_2\text{L}_2$ complexes with monodentate phosphine ligands (Ring = Cp, Cp^* , see sections 2 and 3), we attempted to generate the corresponding $(\text{Ring})\text{MoH}_3\text{L}_2$ by adapting the published procedure.⁴ With frustration, however, we discovered by NMR monitoring that the final reaction mixture contained variable amounts of $(\text{Ring})\text{MoHL}_3$, $(\text{Ring})\text{MoH}_3\text{L}_2$ and even $(\text{Ring})\text{MoH}_5\text{L}$ depending on conditions. A variation of reaction time, solvent, temperature and work-up conditions has not allowed us to obtain a pure crystalline sample of the desired trihydride species from this procedure. As a matter of fact, the use of a large excess of LiAlH_4 in Et_2O at 0°C afforded a pure sample of $\text{Cp}^*\text{MoH}_5(\text{PMe}_3)$ in good yield, see eq. 17,⁸⁴ a compound later prepared also by Parkin by a more economical synthesis from $\text{Cp}^*\text{MoCl}_4(\text{PMe}_3)$.⁵⁴



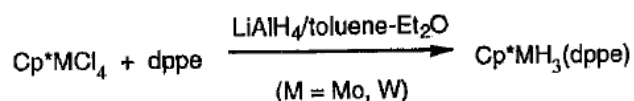
Equation 17

Eventually, suitable conditions were found for the preparation of $\text{CpMoH}_3(\text{PMe}_2\text{Ph})_2$ directly from CpMoCl_3 , PMe_2Ph and LiAlH_4 in THF, eq. 18.⁸⁵ The crude product contained about 12% of the pentahydride complex, but a recrystallization afforded crystals of the pure trihydride. The difficulties associated with the preparation of this system, however, required the development of other systems.



Equation 18

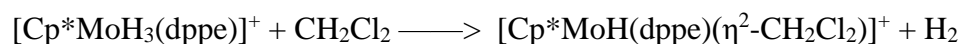
We reasoned that the use of a chelating phosphine should favour the formation of the trihydride over the pentahydride, while using Cp*MoCl₄, as the metal precursor in the presence of the phosphine would offer the convenience of a more straightforward synthesis. For once, we have been rewarded for being daring, compound Cp*MoH₃(dppe) being produced in a single step in a 65% yield according to eq. 19.⁸⁶ Small amounts of the pentahydride by-product, CpMoH₅(η¹-dppe), are also present in solution but do not contaminate the isolated product when using a 80:20 toluene-ether solvent mixture. The use of an ether-richer solvent affords increasing amount of the pentahydride by-product, while using pure toluene requires longer reaction times, eventually leading to other uncharacterized by-products. Of course, this strategy is limited to the Cp* system, given the problems associated with the CpMoCl₄-phosphine interaction (see section 3).



Equation 19

We were also pleased to find that the same strategy of eq. 19 also yields the tungsten analogue. The only other (to the best of our knowledge) previously reported tungsten compound of this family, CpWH₃(PMe₃)₂,⁸⁷ had been synthesized from either W(PMe₃)₅H₂ or W(PMe₃)₄H₄ and cyclopentadiene in poor yields (16%). The use of a toluene-ether mixture is also critical in this case. In addition, the subsequent methanolysis of the excess hydride reagent (which increases the yield without affecting the purity in the Mo case) increases the formation of the pentahydride in the W case. Therefore, the best operating procedure is the immediate isolation of the pure trihydride in ca. 30% yield, followed by methanolysis of the residue to recover additional impure product which can be subsequently recrystallized.

The subsequent chemical and electrochemical oxidation of the Cp*MH₃(dppe) compounds (M = Mo, W) has yielded the corresponding 17-electron [Cp*MH₃(dppe)]⁺ complexes.⁸⁸ Careful kinetic and electrochemical studies in a variety of solvents and conditions have revealed that the Mo complex decomposes by any or a combination of three different mechanisms, each of which has been quantitatively assessed. These are the known deprotonation and disproportionation mechanisms (prevalent in MeCN), plus the heretofore unreported H₂ reductive elimination. The last mechanism is the only one occurring in CH₂Cl₂, leading to a stable 19-electron complex containing a bidentate solvent ligand, as unambiguously shown by Cl hyperfine coupling in the EPR spectrum (eq. 20).⁸⁸



Equation 20

Contrary to the Mo complex, the W analogue does not undergo any decomposition under ambient conditions, allowing the growth of single crystals from MeCN/Et₂O. We expect that the photochemical investigation of this system as well as other similar sterically protected paramagnetic polyhydrides will lead to the discovery of interesting new transformations.

Acknowledgement

I wish to acknowledge the generous support of the Petroleum Research Fund, the National Science Foundation, and the Department of Energy during the period of my association with the University of Maryland at College Park. Work in this area at the Université de Bourgogne is being continued with support from the MENRT and the CNRS. I would like to express my particular gratitude to the Conseil Regional de Bourgogne for providing all the necessary funds for the installation of my new laboratory at the Université de Bourgogne.

References and Notes

- (1) Poli, R. Chem. Rev. 1996, 96, 2135-2204.
- (2) Poli, R.; Wang, L.-S. Coord. Chem. Rev. 1998, 178-179, 169-189.

- (3) Poli, R. *Acc. Chem Res.* 1997, 30, 494-501.
- (4) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. J. *Chem. Soc., Dalton Trans.* 1987, 9-19.
- (5) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inor. Chem.* 1989, 28, 4599-4607.
- (6) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* 1990, 28, 33-37.
- (7) Poli, R.; Mui, H. D. *J. Am. Chem. Soc.* 1990, 112, 2446-2448.
- (8) Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* 1976, 29, 1829-1832.
- (9) Poli, R.; Gordon, J. C. *Inorg. Chem.* 1991, 30, 4550-4554.
- (10) Cotton, F. A.; Poli, R. *Inorg. Chem.* 1987, 26, 1514-1518.
- (11) Owens, B. E.; Poli, R.; Rheingold, A. L. *Inorg. Chem.* 1989, 28, 1456-1462.
- (12) Poli, R.; Kueger, S. T.; Mattamana, S. P. *Inorg. Synth.* 1998, 32, 198-203.
- (13) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* 1990, 29, 2001-2006.
- (14) Falvello, L. R.; Mattamana, S. P.; Poli, R. *Acta Crystollogr, Sect. C* 1995, C51, 569-571.
- (15) Poli, R.; Mattamana, S. P.; Falvello, L. R. *Gazz. Chim. Ital.* 1992, I22, 315-319.
- (16) Mattamana, S. P.; Poli, R. *Inorg. Chim. Acta* 1995, 229, 55-60.
- (17) Green, M. L. H.; Mountford, P. J. *Chem. Soc., Chem. Commun.* 1989, 732-734.
- (18) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* 1964, 1567-1572.
- (19) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* 1985, 4, 953-954.
- (20) Green, M. L. H.; Hubert, J. D.; Mountford, P. J. *Chem. Soc., Dalton Trans.* 1990, 3793-3800.
- (21) Gordon, J. C.; Poli, R. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)*; W. A. Herrmann, Ed.; Georg Thieme Verlag Stuttgart, 1997; Vol. 8; pp 97-98.
- (22) Keogh, D. W.; Poli, R. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)*; W. A. Herrmann, Ed.; Georg Thieme Verlag Stuttgart, 1997; V01. 8; pp 98.

- (23) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* 1942, 22, 69.
- (24) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* 1993, 12, 830-841.
- (25) Abugideiri, F.; Gordon, J. C.; Poli, R.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* 1993, 12, 1575-1582.
- (26) Morise, X.; Green, M. L. H.; McGowan, P. C.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* 1994, 871-873.
- (27) Green, M. L. H.; Morise, X. M.; Hamilton, A. I-1.; Chernega, A. N. *J. Organomet. Chem.* 1995, 488, 73-78.
- (28) Felsberg, R.; Blaurok, S.; Jelonek, S.; Gelbrich, T.; Kirmse, R.; Voigt, A.; Hey-Hawkins, E. *Chem. Ber.* 1997, 130, 807-812.
- (29) Walker, J. D.; Poli, R. *Inorg. Chem.* 1990, 29, 756-761.
- (30) Walker, J. D.; Poli, R. *Inorg. Chem.* 1989, 28, 1793-1801.
- (31) Fettinger, J. C.; Keogh, D. W.; Poli, R. *Inorg. Chem.* 1995, 34, 2343-2347.
- (32) Poli, R.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* 1990, 552-554.
- (33) Feng, Q.; Ferrer, M.; Green, M. L. H.; Mountford, P.; Mtetwa, V. S. B. *J. Chem. Soc., Dalton Trans.* 1992, 1205-1215.
- (34) Linck, R. G.; Owens, B. E.; Poli, R.; Rheingold, A. L. *Gazz. Chim. Ital.* 1991, 121, 163-168.
- (35) Poli, R.; Kelland, M. A. *J. Organomet. Chem.* 1991, 419, 127-136.
- (36) Cole, A.; Gordon, J. C.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* 1992, 11, 1754-1757.
- (37) Poli, R. *Chem. Rev.* 1991, 91, 509-551.
- (38) Gordon, J. C.; Lee, V. T.; Poli, R. *Inorg. Chem.* 1993, 32, 4460-4463.
- (39) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. (A)* 1966, 1966, 1606-1607.
- (40) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. (A)* 1967, 686-687.

- (41) Keogh, D. W.; Poli, R. In *Synthetic Methods of Organometallic and Inorganic Chemistry* (Herrmann/Brauer); W. A. Hermann, Ed.; Georg Thieme Verlag: Stuttgart, 1997; Vol. 8; pp 99-100.
- (42) Poli, R.; Owens, B. E.; Kmegeer, S. T.; Rheingold, A. L. *Polyhedron* 1992, 11, 2301-2312.
- (43) Poli, R.; Krueger, S. T.; Abugideiri, F.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* 1991, 10, 3041-3046.
- (44) Poli, R.; Owens, B. E.; Linck, R. G. *Inorg. Chem.* 1992, 31, 662-667.
- (45) Cole, A. A.; Fettinger, J. C.; Keogh, D. W.; Poli, R. *Inorg. Chim. Acta* 1995, 240, 355-366.
- (46) Wang, L.-S.; Fettinger, J. C.; Poli, R. *J. Am. Chem. Soc.* 1997, 119, 4453-4464.
- (47) Davidson, J. L.; Davidson, K.; Lindsell, W. E.; Murrall, N. W.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1986, 1677-1688.
- (48) Gros, P.; Poli, R. unpublished results.
- (49) Morales, D.; Poli, R.; Richard, P.; Andrieu, J.; Collange, E. *Dalton Trans.* , in press.
- (50) Fromm, K.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem.* 1993, 619, 261-270.
- (51) Poli, R.; Gordon, J.C.; Desai, J.U.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* 1991, 1518-1520.
- (52) Desai, J. U.; Gordon, J. C.; Kraatz, H.-B.; Owens-Waltermire, B. E.; Poli, R.; Rheingold, A. L. *Angew. Chem, Int. Ed. Engl.* 1993, 32, 1486-1488.
- (53) Desai, J. U.; Gordon, J. C.; Kraatz, H.-B.; Lee, V. T.; Owens-Waltermire, B. E.; Poli, R.; Rheingold, A. L.; White, C. B. *Inorg. Chem.* 1994, 33, 3752-3769.
- (54) Shin, J. H.; Parkin, G. *Polyhedron* 1994, 13, 1489-1493.
- (55) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organometal. Chem.* 1978, 157, 239-241.
- (56) Gordon, J. C.; Fanwick, P. E.; Poli, R. *Acta Crystallogr, Sect. C* 1996, C52, 1098-1101.
- (57) Abugideiri, F.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* 1992, 11, 1303-1311.
- (58) Fromm, K.; Plaikner, M.; Hey-Hawkins, E. *Z. Naturforsch.* 1995, 50b, 894-898.

- (59) Cotton, F. A.; Schmid, G. *Polyhedron* 1996, 22, 4053-4059.
- (60) Le Grogneq, E.; Poli, R.; Wang, L.-S., submitted for publication.
- (61) Poli, R.; Wang, L.-S. *Polyhedron* 1998, 17, 3689-3700.
- (62) Jolly, P. W.; Krüger, C.; Romão, C. C.; Romão, M. J. *Organometallics* 1984, 3, 936-937.
- (63) Abugideiri, F.; Keogh, D. W.; Kraatz, H.-B.; Poli, R.; Pearson, W. J. *Organomet. Chem.* 1995, 488, 29-38.
- (64) Fettinger, J. C.; Keogh, D. W.; Poli, R. *J. Am. Chem. Soc.* 1996, 118, 3617-3625.
- (65) Abugideiri, F.; Brewer, G. A.; Desai, J. U.; Gordon, J. C.; Poli, R. *Inorg. Chem.* 1994, 33, 3745-3751.
- (66) Abugideiri, F.; Fettinger, J. C.; Poli, R. *Inorg. Chim. Acta* 1995, 229, 445-454.
- (67) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Bashkin, J.; Derome, A. E.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* 1985, 423-433.
- (68) Segal, J. A.; Green, M. L. H.; Daran, J.-C.; Prout, K. J. *J. Chem. Soc., Chem. Commun.* 1976, 766-768.
- (69) Green, M. L. H.; Knight, J.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* 1977, 2189-2195.
- (70) Green, M. *Polyhedron* 1986, 5, 427-433.
- (71) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1983, 927-939.
- (72) Caulton, K. G. *New J. Chem.* 1994, 18, 25-41.
- (73) Tudoret, M.-J.; Robo, M.-L.; Lapinte, C. *Organometallics* 1992, 11, 1419-1422.
- (74) Abugideiri, F.; Fettinger, J. C.; Keogh, D. W.; Poli, R. *Organometallics* 1996, 15, 4407-4416.
- (75) Abugideiri, F.; Keogh, D. W.; Poli, R. *J. Chem. Soc., Chem. Commun.* 1994, 2317-2318.
- (76) Keogh, D. W.; Poli, R. *J. Am. Chem. Soc.* 1997, 119, 2516-2523. 1993, 12, 2388-2389.
- (77) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A. *J. Chem. Soc., Chem. Commun.* 1997, 839-890.

- (78) Poli, R.; Quadrelli, E. A. *New J. Chem.* 1998, 22, 435-450.
- (79) Ryan, O.B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* 1990, 115, 1581-1594.
- (80) Pilloni, G.; Schiavon, G.; Zotti, G.; Zecchin, S. *J. Organomet.* 1985, 1383-1384.
- (81) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A.; Torralba, R. C. *Organometallics* 1998, 17, 5767-5775.
- (82) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A. *J. Chem. Soc., Dalton Trans.* in press.
- (83) Aviles, T.; Green, M. L. H.; R., D. A.; Romão, C. *J. Chem. Soc., Dalton Trans.* 1979, 1367-1371.
- (84) Abugideiri, F.; Kelland, M. A.; Poli, R. *Organometallics*, 1993, 12, 2388-2389.
- (85) Abugideiri, F.; Fettinger, J. C.; Pleune, B.; Poli, R.; Bayse, C. A.; Hall, M. B. *Organometallics* 1997, 16, 1179-1185.
- (86) Pleune, B.; Poli, R.; Fettinger, J. C. *Organometallics* 1997, 16, 1581-1594.
- (87) Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* 1985, 1383-1384.
- (88) Pleune, B.; Morales, D.; Meunier-Prest, R.; Richard, P.; Collange, E.; Fettinger, J. C.; Poli, R. *J. Am. Chem. Soc.* in press.

Biographical Sketch

Rinaldo Poli received a Laurea degree in Chemistry from the University of Pisa (1981) and a Ph.D. from the Scuola Normale Superiore, Pisa (1985) under the supervision of Fausto Calderazzo. In between, he spent a mandatory year in the Army and one year as an exchange student at the Imperial College of Science and Technology in London with Geoffrey Wilkinson. After two years of postdoctoral employment at Texas A&M University with Al Cotton, he was appointed Assistant Professor (1987) at the University of Maryland, College Park, being promoted to Associate Professor in 1992 and to Professor in 1995. In 1996, he moved to his current position as Professor at the Université de Bourgogne. He has been a visiting professor

in Munich (Humboldt Forschungsstipendiat, 1993-94), at the Tokyo Metropolitan University (1996) and at the Inorganic Chemistry Laboratory in Oxford (1998). Other recognitions received are a Dreyfus New Faculty Award (1987), the Presidential Young Investigator Award (1990), the Alfred P. Sloan Foundation Research Fellowship (1992), and the Medaglia R. Nasini from the Italian Chemical Society (1992).