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Ruthenium and Osmium Metalloradicals

Rinaldo Poli*

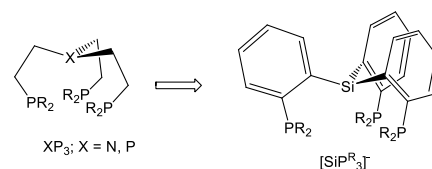
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Ruthenium · Osmium · Dinitrogen · Radicals · Non-innocent ligands

With a limited number of well-understood exceptions (the square planar d^8 configuration, complexes with strongly π -donating ligands, ...), complexes of transition metals that belong to the $4d$ and $5d$ series most typically follow the so-called EAN rule by adopting a closed-shell 18-electron configuration. Relative to the $3d$ metals, those of the $4d$ and $5d$ series possess more diffuse and more polarizable d orbitals, leading to greater bond covalence and to lower pairing energies and consequently to lower stability for open-shell configurations, especially in the lower oxidation states and especially for the late transition metals.^[1] Coordinative saturation is achieved by coordination of a suitable number of 1- and 2-electron ligands and/or by forming metal-metal bonds in oligonuclear clusters. Nevertheless, enforcing mononuclear metalloradical configurations through the use of specially designed ligands can lead to peculiar properties and reactivity. A good example is the use of bulky porphyrins or geometrically constrained alkene-containing ligands leading to stable (porphyrin)Rh^{II} complexes or (alkene)Rh^{II} and (alkene)Ir^{II} complexes that have shown interesting applications in C-H activation and in catalysis.^[2, 3]

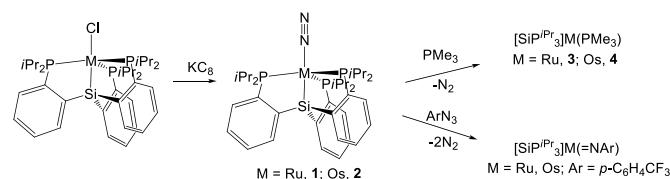
For the heavier Group 8 elements ruthenium and osmium, complexes with the formal oxidation state I and a metalloradical character were previously produced, generally by electrochemical methods, only as unstable species or could not be isolated. Pilloni *et al.* already pointed out in 1977 that the coordination geometry could be an important factor allowing the generation of stable d^7 mononuclear complexes and that the presumed lability of the chloride ligand in complex [Ru(dppp)₂Cl] (dppp = 1,3-bisdiphenylphosphinopropane) opens decomposition pathways through disproportionation.^[4] A longer-living but still not isolable Ru^I complex, [Ru(PP₃)Cl],^[5] was obtained by using the “Sacconi-type” tetradentate phosphine ligand PP₃ = P(CH₂CH₂PPh₂)₃, which is known to stabilize M(L₄) moieties either in an octahedral (with two additional *cis* ligands) or in a trigonal bipyramidal (with one additional *axial* ligand) geometry. A key to further stabilize the construct could be the incorporation of the anionic function into the tetradentate ligand to yield a M(XL₃) moiety. On the basis of this idea, Peters has recently developed tris(phosphino)silyl ligands, the relationship with the Sacconi system being illustrated in Scheme 1, initially showing that they are capable of stabilizing dinitrogen

complexes of Fe^I, [(SiP^R₃)Fe(N₂)], with R = Ph or *i*Pr.^[6-8]



Scheme 1. Relationship between Sacconi-type XP₃ and Peter's [SiP^R₃] ligands.

More recently, the same ligand (with R = *i*Pr) has successfully been used to generate the first stable mononuclear Ru^I and Os^I metalloradicals (see Scheme 2).^[9] The precursor complexes [(SiP^{*i*Pr}₃)MCl] were prepared from [(η⁶-C₆H₆)MCl₂]₂ and HSiP^{*i*Pr}₃ in the presence of Et₃N and then converted into [(SiP^{*i*Pr}₃)M(N₂)] (M = Ru, **1**; Os, **2**) by reduction with KC₈ under dinitrogen.



Scheme 2. Generation and reactivity of [SiP^{*i*Pr}₃]M(N₂) complexes of ruthenium and osmium.

The spectroscopic (IR, NMR, EPR) and structural (single crystal X-ray diffraction, see Figure 1 for **1**) characterization leaves no doubt about the formulation as mononuclear M^I species. The N₂ ligand is labile and could be substituted by PMe₃ yielding the corresponding [(SiP^{*i*Pr}₃)M(PMe₃)] complexes (M = Ru, **3**; Os, **4**), which have also been fully characterized. The two dinitrogen complexes were also investigated electrochemically, revealing a reduction and an oxidation. The reduction process is reversible for both compounds and the stable M⁰ products could be generated by stoichiometric reductions with KC₈, isolated and crystallographically characterized. The oxidation process is reversible only for Ru and the stable product, containing however a very labile N₂ ligand, could be obtained by stoichiometric oxidation with [Cp₂Fe][B{C₆H₃(CF₃)₂-3,5}₄]. The radical character at the metal is indicated by the chemical reactivity for compound **1**, *i.e.* by the generation of the Ru^{II} complexes [(SiP^{*i*Pr}₃)RuH(N₂)], [(SiP^{*i*Pr}₃)RuI] and [(SiP^{*i*Pr}₃)Ru(SPh)] upon treatment with Bu₃SnH, I₂ and PhSSPh, respectively. However, two-electron reactivity is also shown, in addition to the above described transformation to **3** and **4**, by the reaction with organoazides, leading to imido/nitrene products via elimination of N₂ (Scheme 2). The EPR investigation and DFT calculations for compounds **1-4** give strong support to the description of the complexes as *bona fide* metalloradicals. The EPR

[*] Prof. R. Poli
CNRS; LCC (Laboratoire de Chimie de Coordination);
Université de Toulouse; UPS, INPT; 205, route de
Narbonne, F-31077 Toulouse, France, and Institut
Universitaire de France, 103, bd Saint-Michel, 75005
Paris, France.
Fax: (+)33-561553003
E-mail: rinaldo.poli@lcc-toulouse.fr
Homepage: http://www.lcc-toulouse.fr/equipe_g/pages/poli/index.html

spectrum shows significantly anisotropic rhombic tensors with larger ($g_{\max}-g_{\min}$) values than typically observed for ligand-centered radicals, while the calculations place the majority of the spin density (76% for **1**, 69% for **2**, 84% for **3** and 79% for **4**) on the metal and also a non negligible fraction at the P nuclei (Figure 1). The observed P hyperfine splitting is consistent with the unpaired electron being located in the equatorial plane.

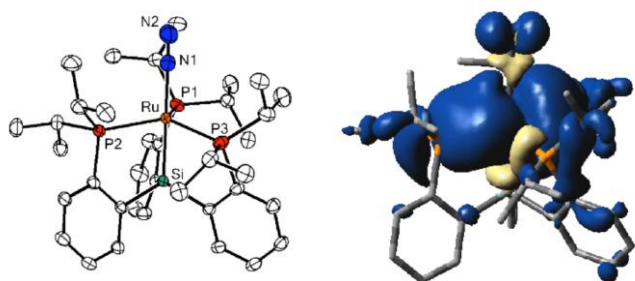
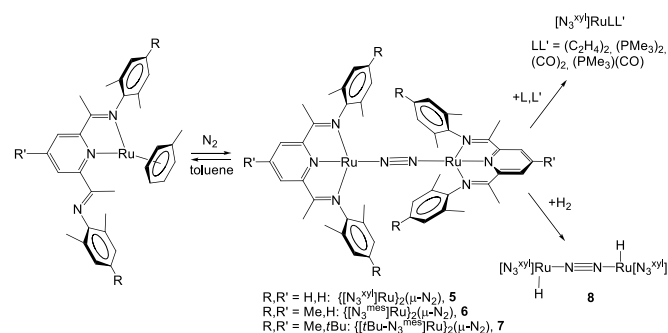


Figure 1. X-ray structure and spin density plot for compound **1**.

Another recent study by Berry^[10] has shown that the Ru⁰ complexes (η^6 -toluene)Ru[N₃] ([N₃] = 2,6-diiminopyridine), where [N₃] is only coordinated in a bidentate fashion, are converted under dinitrogen to the diamagnetic dinuclear {[N₃Ru]₂(μ -N₂)} complexes **5-7**, Scheme 3, where the coordination geometry of the Ru center is strictly square planar, an unusual observation for a formally Ru⁰ center. In light of the known non-innocent character of 2,6-diiminopyridine ligands and on the previous recognition that related [N₃]FeCl and [N₃]Fe(N₂)₂ complexes are best described as Fe^{II} complexes with transfer of one or two electrons to the ligand,^[11, 12] the electronic structure of compounds **3-5** has been carefully analyzed. Structural evidence (ligand imino C=N distances) and an unusual temperature independent shift of the imine Me proton resonance in the ¹H NMR spectrum suggest a certain degree of ligand non-innocence. Replacement of the N₂ ligand in compound **5** by other neutral donors (C₂H₄, PMe₃, CO) yields 5-coordinate complexes [N₃^{xy}]RuLL' (Scheme 3) that seem adequately described as Ru⁰ derivatives. On the other hand, the addition of H₂ affords an unusual dinuclear Ru hydride complex {[N₃^{xy}]RuH}₂(μ -N₂), **8** (see Scheme 3), the structure of which shows two square pyramidal Ru centers with an axial hydrido ligand, linked by a linear N₂ bridge.^[13] This is formally a Ru^I species and is indeed paramagnetic as expected for one unpaired electron per [N₃^{xy}]Ru(H) unit, but displays no tendency to further add H₂ to yield a dihydrido Ru^{II} product. Broken symmetry DFT calculations on a mononuclear [N₃^{xy}]Ru(H)(N₂) model complex reveal a large contribution of the Ru^{II}/[N₃⁻] formalism, with 73% SOMO localization on the [N₃] ligands and only 19% on the metals. In conclusion, the one-electron reactivity of **5** with H₂ appears more consistent with a formal transformation of Ru^I to Ru^{II} rather than Ru⁰ to Ru^I.

In conclusion, the two above-highlighted elegant studies by Peters and Berry have underlined for the first time that relatively stable complexes of ruthenium and osmium in the oxidation state I may be obtained by judicious choice of the supporting ligand system, but also that internal electronic rearrangements are possible when the ligand has the ability to play a non innocent role. They have clearly shown the need to carefully apply a vast array of experimental and theoretical characterization methods for achieving

an appropriate description of the electronic structure for these interesting new systems.^[9, 10, 13] The preliminary reactivity studies reported in these contributions already announce that they are amenable to the development of interesting new chemistry. Note that a recent review on ruthenium complexes with non innocent ligands has appeared,^[14] although it makes no mention of systems best described as having a Ru center with a formal oxidation state of I.



Scheme 3. Generation and reactivity of [SiP^{Pr}₃]M(N₂) complexes.

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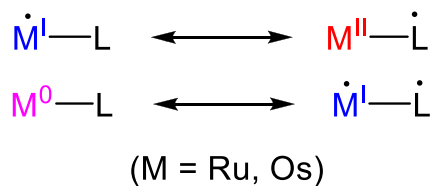
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News on Ruthenium and Osmium
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Unprecedented stability for ruthenium(I) and osmium(I) complexes with metalloradical character has been achieved by use of judiciously chosen supporting ligands based on the tris(phosphino)silyl motif, but pronounced radical character on Ru^I is also enforced by non-innocent ligands of diiminopyridine type.