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Amal Bouammali, Christian Bijani, Laure Vendier, Michel Etienne, Antoine Simonneau. Reaction of Methyllithium with Group 6 Phosphine Dinitrogen Complexes. *European Journal of Inorganic Chemistry*, 2020, Nitrogen Fixation, 2020 (15-16), pp.1423-1427. 10.1002/ejic.201901346 . hal-02611054

HAL Id: hal-02611054

<https://hal.science/hal-02611054>

Submitted on 9 Nov 2020

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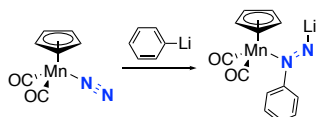
Reaction of Methylolithium with Group 6 Phosphine Dinitrogen Complexes

Amal Bouammali,^[a] Christian Bijani,^[a] Laure Vendier,^[a] Michel Etienne,^[a] and Antoine Simonneau^{*[a]}

Abstract: The reaction of MeLi with several group 6 phosphine end-on dinitrogen complexes of the general formula $[\text{ML}_4(\text{N}_2)_2]$ ($\text{M} = \text{Mo}$ or W) is reported. Unlike the isoelectronic complex $[\text{CpMn}(\text{CO})_2(\text{N}_2)]$ on which RLi reagents have been reported to add to the N_2 ligand, we show herein that MeLi attacks the metal centre to afford rare anionic *trans* methyl dinitrogen complexes.

Introduction

Dinitrogen has a very rich coordination chemistry that has been widely explored for more than 50 years.^[1–4] The development of this field is linked to the problems raised by nitrogen fixation into the biosphere: indeed, dinitrogen complexes have proven valuable models in order to understand the functioning of the nitrogenases.^[5–7] Besides, the environmental and sustainability concerns linked to anthropogenic N fixation via the Haber-Bosch process^[8–11] have fueled a quest for bio-inspired molecular alternatives.^[12–15] Among all the dinitrogen complexes found in the literature, a very common coordination mode is the terminal one. Hidai-Chatt group 6 complexes may be the most emblematic compounds of this type. Their reactivity has been extensively studied, and due to the polarization induced by coordination as well as back-donation from the metal, electrophilic attack at the terminal N (N_β) is generally observed.^[16] This has served as starting point for the development of synthetic methods affording nitrogen compounds such as ammonia,^[12–15] silylamines^[17] or more complex organonitrogen products.^[16] Contrastingly, nucleophilic attack at N_α has been rarely encountered. As far as we are aware, Sellmann's complex $[\text{CpMn}(\text{CO})_2(\text{N}_2)]$ remains the sole compound for which such reactivity has been reported, using organolithium reagents as nucleophiles to afford an akyldiazenido ligand (Scheme 1).^[18] This is reminiscent of the reactivity of the isoelectronic CO ligand that leads to Fischer carbenes for example.^[19] In the present article, we explore the reactivity of some Mo and W Hidai-Chatt-type complexes, isoelectronic to $[\text{CpMn}(\text{CO})_2(\text{N}_2)]$, with methylolithium, in order to verify whether the same outcome than with Sellmann's Mn complex is observed.



Scheme 1. Nucleophilic attack at an end-on N_2 ligand in $[\text{CpMn}(\text{CO})_2(\text{N}_2)]$.

Results and Discussion

We chose to investigate the reactivity of the complexes *trans*- $[\text{M}(\text{N}_2)_2(\text{dppe})_2]$ **1** [$\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane], *trans*- $[\text{M}(\text{N}_2)_2(\text{depe})_2]$ **2** [$\text{depe} = 1,2$ -bis(diethylphosphino)ethane] and $[\text{M}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ ($\text{M} = \text{Mo}$, **3_{Mo}**, 12:88 *cis/trans* mixture, or W , **3_W**, only *cis*). The reaction of **1_{Mo}** with 1 equiv. of MeLi (1.6 M in Et_2O) at room temperature yields small amounts of a new diamagnetic species **4_{Mo}** along with untouched **1_{Mo}**. More forcing conditions (2 equiv. MeLi, 50 °C) allowed us to fully convert **1_{Mo}** to **4_{Mo}**. In this new compound all phosphorus atoms remained magnetically equivalent, while a shielded CH_3 signal at -2.94 ppm was observed in ^1H NMR as a quintet ($^3J_{\text{HP}} = 6$ Hz). A ^{13}C NMR experiment revealed the associated carbon signal at -4.1 ppm (quint, $^2J_{\text{CP}} = 9$ Hz). **4_{Mo}** could be isolated by precipitation from pentane at -40 °C as a dark red powder (ca. 68% yield). It is highly sensitive to air or moisture, does not stand in solution upon exposure to vacuum and decomposes slowly in the solid state even when stored in the -40 °C freezer of the glove box. Therefore, its handling was challenging and its full characterization made difficult. The infrared spectrum (ATR) of isolated **4_{Mo}** shows a strong absorption band at 1780 cm^{-1} that can be attributed to a ν_{N_2} stretching vibration, and nitrogen was detected in non-negligible amounts when we attempted its elemental analysis, suggesting **4_{Mo}** has likely retained one N_2 ligand in its coordination sphere. From these pieces of data we propose that the organolithium reagent reacted with the metal center instead of the N_2 ligand, affording an anionic *trans*-methyl dinitrogen complex. Integration of the THF signals in ^1H NMR revealed exactly 3 equivalents remained in the isolated powder: thus, it is reasonable to propose that the Li atom is bound to 3 THF molecules and the terminal nitrogen of an end-on N_2 ligand.^[20] As the outcome of an attempt to crystallize **4_{Mo}**, we have serendipitously obtained good quality crystals of the *ortho*-metallated complex **5_{Mo}** (Fig. S27), but the inherent reactivity of **4_{Mo}** prevented the growth of single crystals suitable for X-ray analysis. **5_{Mo}** presumably arise from *ortho*-C–H activation concomitantly with methane evolution.^[21] However, we were not able to find conditions in which **5_{Mo}** could be formed in high yields, which precluded further characterization. Likewise, the depe-supported complex **2_{Mo}** fully reacted in the presence of an excess of MeLi (4 equiv.) in THF at 60 °C to afford the depe analog of **4_{Mo}**, **6_{Mo}** (Scheme 2). The latter did not exhibit improved stability compared to **4_{Mo}**. Although clean reaction mixtures were obtained under these conditions, its co-precipitation with excess MeLi hampered isolation of **6_{Mo}** in pure form.

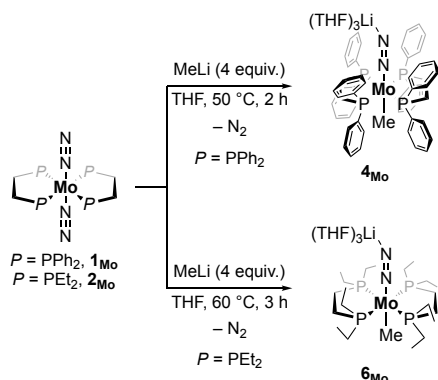
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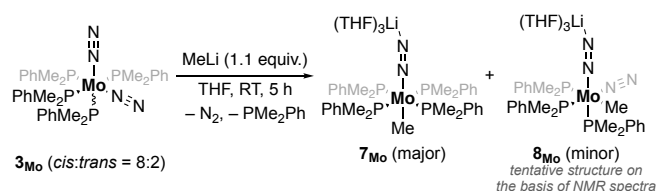
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Scheme 2. Reactions of **1_{Mo}** and **2_{Mo}** with MeLi affording anionic *trans*-methyl dinitrogen complexes.

Next, a mixture of *cis*- and *trans*-**3_{Mo}** supported by the PMe_2Ph monophosphine was treated with MeLi. **3_{Mo}** reacted cleanly in the presence of 1.1 equiv. of MeLi to afford the *trans*-methyl complex **7_{Mo}** as the major compound, which was characterized by a highfield-shifted quintet in ^1H NMR at $\delta -1.38$ ppm ($^3J_{\text{HP}} = 7$ Hz). Along **7_{Mo}**, another minor methyl complex (**8_{Mo}**) formed (ca. 8:2 ratio according to ^1H NMR). Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two sets of inequivalent phosphorus atoms and integration was in agreement with the loss of one phosphine (see Fig. S20). A CH_3 signal in ^1H NMR with an observed quartet multiplicity ($\delta -1.47$ ppm, $^3J_{\text{HP}} = 7$ Hz) was present in ^1H NMR; selective irradiation on each of the ^{31}P resonances indeed showed this signal was actually a dt (Fig. S17). A DOSY experiment resulted in close diffusion coefficients for **7_{Mo}** and **8_{Mo}**, while a EXSY experiment did not show any exchange between them (Fig. S18). Because separation of the two species was not possible, further characterization of **8_{Mo}** could not be performed. Yet, on the basis of NMR data, we propose **8_{Mo}** to be *fac*-[(PMe_2Ph)₃MoMe(N_2)₂Li] (Scheme 3).



Scheme 3. Reactivity of complex **3_{Mo}** with MeLi.

Unlike their molybdenum analogues, **1_W** and **2_W** did not react with MeLi under the conditions described above. In the presence of excess MeLi and at elevated temperature (80 °C), slow decomposition occurred instead, with no evidence of tungsten methyl complexes according to NMR data. Yet, treatment of **3_W** with MeLi led to a mixture of compounds in which a major tungsten complex **9_W** was found, according to the $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of an aliquot. The latter was characterized by a ABX_2 system ($^2J_{\text{PP}} = 14$ and 18 Hz). Important amounts of free PMe_2Ph were also found, suggesting facile phosphine dissociation. Precipitation of **9_W** in low amounts (8%) out of the reaction medium in crystalline form allowed its characterization by X-ray diffraction.^[22] One of the aromatic substituent of a phosphine ligand is *ortho*-metallated in **9_W**, yielding a structure highly distorted from an ideal octahedron (Figure 1), akin to **5_{Mo}** (Fig. S27). ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction run in

[D₈]THF (Fig. S23–24) indeed shows the presence of methyl residues bound to a $\text{W}(\text{PMe}_2\text{Ph})_4$ core in small amounts, the major one being characterized by a quintet in ^1H NMR ($\delta -1.06$ ppm, $^3J_{\text{HP}} = 7$ Hz) to which we associated a singlet in $^{31}\text{P}\{^1\text{H}\}$ NMR ($\delta -20.9$ ppm): this compound may be **7_W**. Although formed early on, **7_W** disappeared as **9_W** formed. Methane build-up was also observed: thus, we speculate that **9_W** results from the *ortho*-metallation of the phosphine ligand in a $\text{W}-\text{CH}_3$ intermediate. Other minor diamagnetic W species were also present in the reaction mixture but could not be identified. In addition, PMe_3 was also detected. It is probably formed by the reaction of free PMe_2Ph with excess MeLi.^[23]

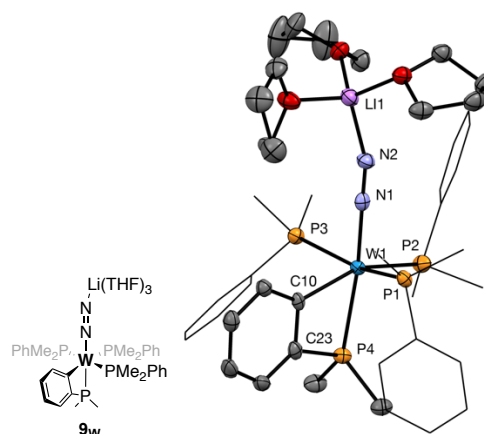
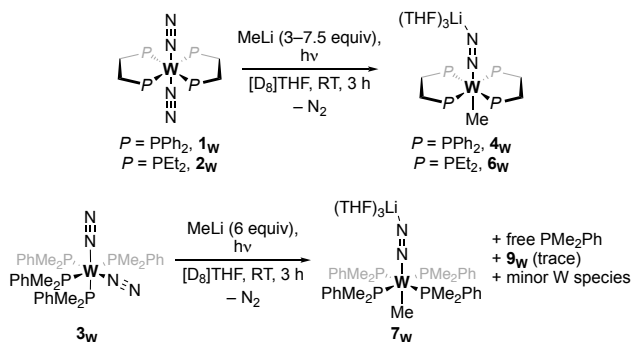


Figure 1. Molecular structure of compound **9_W** in the solid state. Hydrogen atoms omitted for clarity, ellipsoids drawn at the 50% probability level. Relevant bond lengths (Å) and angles (°): N2–Li1 1.935(6); N1–N2 1.175(4); W1–N1 1.913(3); W1–C10 2.230(3); W1–P1 2.397(1); W1–P2 2.424(1); W1–P3 2.405(1); W1–P4 2.519(1); N1–N2–Li1 161.4(3); W1–N1–N2 178.8(2); P4–W1–C10 64.32(8); W1–C10–C23 107.2(2); W1–P4–C23 85.1(1); P4–C23–C10 103.3(2); N1–W1–C10 107.3(1).

The lack of reactivity of **1_W** and **2_W** may stem from their inability to thermally dissociate N_2 . Indeed, we suggest the formation of **4_{Mo}**, **6_{Mo}** and **7_{Mo}** occurs after dissociation of one N_2 ligand,^[24] which liberates a vacant coordination sites, thus setting the stage for the carbanion to attack at the metal. The thermal activation coupled to the overall long reaction times reflects the reported low rate of N_2 dissociation.^[25] However, the tungsten complexes readily photodissociate N_2 , and their treatment with excess MeLi under irradiation allowed us to detect the methyl-dinitrogen complexes **4_W**, **6_W** and **7_W** as the major components of the reaction mixtures. **4_W** and **6_W** were formed quantitatively according to NMR, but akin to the molybdenum compounds, their isolation in pure form proved difficult owing to their sensitivity to vacuum and limited stability in the solid state. **7_W** formed in a few hours in mixture with free PMe_2Ph as well as other minor complexes as shown by NMR monitoring (Scheme 4 and Fig. S25–26). Attempts to isolate it have resulted in mixture where **7_W** had partially degraded to another, unidentified methyl complex.



Scheme 4. Reactions of **1w**, **2w** and **3w** with MeLi under irradiation (460 nm) affording anionic *trans*-methyl dinitrogen complexes.

When the more sterically demanding organolithium reagents *n*-BuLi or PhLi were employed, no evidence of RLi reaction with the metal complex could be observed by monitoring these reactions by NMR spectroscopy. The alkylating agent Me₂Mg did not react with **3Mo**, even under forcing conditions (60 °C, 6 h).

Conclusions

Despite the demonstration more than 40 years ago that polar organometallic reagents, and especially MeLi, can attack coordinated dinitrogen in [CpMn(CO)₂(N₂)] (Scheme 1),^[18] the corollary for the isoelectronic, zero-valent group 6 [M(N₂)₂L₄] complexes **1–3** is not true. Such discrepancy might stem from the difference in electron back-donation to the N₂ ligand that can be related to the ν_{NN} stretching frequencies: 2169 cm^{−1} for [CpMn(CO)₂N₂], and between 2020 and 1891 cm^{−1} for **1–3**: the N₂ ligand is thus more likely to show “electrophilic” character in the former. Under thermal (Mo) or photochemical (W) activation, MeLi was found to attack at the metal by dissociative displacement of one of the N₂ ligands, a behavior that can be paralleled to the one of W(0)-nitrosyl-carbonyl complexes.^[26] Rare, low valent and very labile methyl-dinitrogen complexes^[27–30] are thus obtained.

Experimental Section

General Information: All reactions were performed in flame- or oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen filled *Jacomex* glove box (O₂ < 0.5 ppm, H₂O < 1 ppm). Photochemical reactions were performed by irradiating glass NMR tubes or Schlenk flasks in a cylinder covered with 20W blue LEDs strips (λ_{max} = 460 nm) and topped with a ventilator. Solvent used were pre-dried (THF and *n*-pentane by passing through a Puresolv MD 7 solvent purification machine; *n*-hexane by distillation over CaH₂), degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. [D₈]THF (purchased from *Eurisotop*) was degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. *trans*-[M(dppe)₂(N₂)₂] (**1**), *trans*-[M(depe)₂(N₂)₂] (**2**) and *cis/trans*-[M(PMe₂Ph)₄(N₂)₂] (**3**) with M = Mo or W were prepared according to reported procedures.^[31] Methylolithium (1.6 M in Et₂O) was purchased from Sigma-Aldrich and was titrated before use.^[32] ¹H, ¹³C, and ³¹P NMR spectra were recorded in [D₈]THF using NMR tubes equipped with J. Young valves on a Bruker Avance III 400 spectrometer or Avance NEO 600. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard (C₄H₉D₇O: δ reported = 3.58 and 1.72 ppm for ¹H NMR; 67.2 and 25.3 for ¹³C NMR). ³¹P NMR spectra were calibrated according to the IUPAC recommendation.^[33] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constant (Hz), and

integration. Infrared (IR) spectra were recorded in the glove box on an Agilent Cary 630 FT-IR spectrophotometer equipped with ATR or transmission modules and are reported in wavenumbers (cm^{−1}) with (s) indicating strong absorption. We draw the attention of the reader that all compounds described herein are highly sensitive and do not tolerate vacuum (nor light for **7Mo**), making their isolation in analytically pure form challenging; most of our attempts to obtain and analyze crystals were scuppered by the reactivity of the compounds. Consequently, none of the samples we submitted for elemental analysis (performed on samples sealed in tin capsules under Ar or N₂ by the Analytical Service of the Laboratoire de Chimie de Coordination) gave satisfying results.

***trans*-[MeMo(dppe)₂N₂]Li(THF)₃ (**4Mo**):** To a stirred solution of **1Mo** (0.127 g, 0.133 mmol) in THF (2.5 mL) in a screw-cap 10-mL Schlenk tube, an ether solution of MeLi (1.6 M, 0.33 mL, 0.532 mmol, 4 equiv.) was added dropwise and the obtained mixture was stirred at 50 °C for 2 h under a nitrogen atmosphere. After cooling the solution to room temperature, the reaction flask was brought to the glove box where pentane (15 mL) was added and the resulting mixture was kept at −40 °C for 1 h which caused the precipitation of **4Mo** as a dark red powder. This product was recovered by filtering off the supernatant, washed with pentane (2 mL) and briefly under an N₂ stream to partly remove remaining pentane as the compound is vacuum sensitive; this did not allow to get a pentane-free product. Approximate yield deduced from NMR was 68% (0.105 g, 0.091 mmol). **¹H-NMR** (400 MHz, [D₈]THF) δ = 7.70 (d, *J* = 5.8 Hz, 8H_{meta}), 7.11 – 6.98 (m, 8H_{ortho} + 4H_{para}), 6.88 (t, *J* = 7.2 Hz, 4H_{para}), 6.77 (t, *J* = 7.5 Hz, 8H_{ortho}), 6.72 – 6.65 (m, 8H_{meta}), 2.50 – 2.29 (m, 4H, CH₂), 2.06 – 1.90 (m, 4H, CH₂), −2.94 (quint, ³J_{HP} = 6.3 Hz, 3H, MoCH₃). **¹³C{¹H}-NMR** (100 MHz, [D₈]THF) δ = 145.6 (quint, *J*_{CP} = 4.5 Hz, 4C_{ipso}), 142.4 (quint, *J*_{CP} = 5.4 Hz, 4C_{ipso}), 135.2 (t, *J*_{CP} = 3.0 Hz, 8C_{meta}), 133.1 (8C_{meta}), 127.2 (4C_{para}), 127.1 (8C_{ortho}), 126.9 (8C_{ortho}), 126.2 (4C_{para}), 30.9 (p, *J*_{CP} = 9.2 Hz, 2CH₂), −4.1 (quint, ²J_{CP} = 8.5 Hz, MoCH₃). **³¹P{¹H}-NMR** (162 MHz, [D₈]THF) δ = 73.7. **IR** (ATR) ν_{NN} = 1784 cm^{−1} (s). **Elem. Anal.** calcd for C₆₅H₇₂LiMoN₂O₃P₄: C, 67.53; H, 6.28; N, 2.42. Found: C, 63.88; H, 6.26; N, 2.9.

***trans*-[MeW(dppe)₂N₂]Li(THF)₃ (**4w**):** To a solution of **1w** (0.037 g, 0.036 mmol) in [D₈]THF (0.7 mL) in a Young NMR tube, an ether solution of MeLi (1.6 M, 70 μL, 0.11 mmol, 3.0 equiv) was added dropwise and the obtained orange mixture was stirred under irradiation at 460 nm for 3 h under an argon atmosphere. Pentane (15 mL) was added and the resulting mixture was stored at −40 °C for 1 h which caused the precipitation of a red solid. This solid was washed with pentane (2 × 2 mL) and dried briefly under an N₂ stream to partly remove remaining pentane as the compound is vacuum sensitive; this did not allow to get a pentane-free product. Approximate yield deduced from NMR was 91% (0.040 g, 0.032 mmol). **¹H-RMN** (400 MHz, [D₈]THF) δ = 7.75–7.63 (m, 8H, H_{meta}); 7.04 (m, 12H, H_{para+ortho}), 6.86 (t, 4H, *J* = 7.2 Hz, H_{para}), 6.77 (t, *J* = 7.4 Hz, 8H_{ortho}), 6.68–6.59 (m, 8H, H_{meta}), 2.49–2.29 (m, 4H, CH₂), 2.09–1.84 (m, 4H, CH₂), −2.81 (quint, ³J_{HP} = 7.0 Hz, 3H, WCH₃). **¹³C{¹H}-NMR** (100 MHz, [D₈]THF) δ = 145.8 (quint, *J*_{CP} = 6.2 Hz, C_{ipso}), 142.0 (quint, *J*_{CP} = 6.8 Hz, C_{ipso}), 135.8–135.7 (m, 8C_{meta}), 133.4–133.3 (m, 8C_{meta}), 127.5–127.4 (m, 8C_{ortho}), 127.2–127.1 (m, 8C_{ortho}), 126.2 (s, 4C_{para}), 32.9 (quint, *J*_{CP} = 9.7 Hz, 4C, PCH₂), −6.3 (quint, ²J_{CP} = 6.0 Hz, WCH₃). **³¹P{¹H}-NMR** (162 MHz, [D₈]THF) δ = 51.3 (*J*_{PW} = 310 Hz). **IR (ATR)** ν_{NN} = 1763 cm^{−1} (s). **Elem. Anal.** calcd for C₆₅H₇₂LiWN₂O₃P₄: C, 62.76; H, 5.83; N, 2.25. Found: C, 57.48; H, 6.08; N, 1.54.

***trans*-[MeMo(depe)₂N₂]Li(THF)₃ (**6Mo**):** To a stirred solution of **2Mo** (0.080 g, 0.142 mmol) in THF (1.5 mL) in a screw-cap 10-mL Schlenk tube, an ether solution of MeLi (1.6 M, 0.35 mL, 0.57 mmol, 4.0 equiv.) was added dropwise and the obtained mixture was stirred at 60 °C for 3 h under a nitrogen atmosphere. After cooling the solution to room temperature, the reaction flask was brought to the glove box where pentane (15 mL) was added and the resulting mixture was kept at −40 °C overnight which caused co-precipitation of excess MeLi together with **6Mo** as orange crystals. The solids were recovered by filtration, washed with pentane (2 × 2 mL) and ether (2 mL) and dried briefly under an N₂ stream. **6Mo** was obtained as an orange solid in mixture with MeLi. Approximate yield deduced from NMR was 60% (0.066 g, 0.085 mmol). **¹H-NMR** (400 MHz, [D₈]THF) δ = 1.90 (q, *J* = 7.4 Hz, 8H), 1.67 (ddq, *J* = 21.7, 14.7, 7.1 Hz, 8H, CH₂), 1.42 – 1.23 (m, 8H, CH₂), 1.06 – 0.98 (m, 12H), −2.56 (quint, *J* = 6.5 Hz, 3H, MoCH₃); one of the CH₂CH₃ signals overlap with the one of Et₂O.

$^1\text{H}\{^3\text{P}\}$ -NMR (400 MHz, $[\text{D}_8]\text{THF}$) δ = 1.90 (qd, J = 7.6, 2.6 Hz), 1.67 (ddq, J = 21.7, 14.7, 7.5 Hz), 1.40 – 1.26 (m), 1.10 (t, J = 7.6 Hz), 1.02 (t, J = 7.6 Hz), –2.56 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100 MHz, $[\text{D}_8]\text{THF}$) δ = 24.7 (quint, J_{CP} = 8.8 Hz, 4C, PCH_2), 21.5 (dt, J_{CP} = 18.2, 2.6 Hz, 4C, PCH_2CH_3), 9.8 (4C, CH_3), 9.3 (4C, CH_3), –16.5 (quint, $^2J_{\text{CP}}$ = 9.4 Hz, MoCH_3). **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (162 MHz, $[\text{D}_8]\text{THF}$) δ = 60.8. **IR (ATR)** $\nu_{\text{N-N}}$ = 1755 cm^{-1} (s).

***trans*-[MeW(depe) $_2\text{N}_2$ Li(THF) $_3$ (6w):** To a solution of **2w** (0.070 g, 0.107 mmol) in $[\text{D}_8]\text{THF}$ (0.7 mL) in a Young NMR tube, an ether solution of MeLi (4.6 M, 110 μL , 7.50 equiv) was added dropwise and the obtained orange mixture was stirred under irradiation at 460 nm for 3 h under a argon atmosphere. In a glove box, the solution was transferred to a 20-mL screw-cap tube (1 mL of THF was used to rinse the NMR tube) and pentane (15 mL) was added. The resulting mixture was stored at –40 °C overnight which caused the co-precipitation of excess MeLi together with **4w** as orange crystals. The solids were recovered by filtration, washed with pentane (2 \times 2 mL) and ether (2 mL) and dried briefly under an N_2 stream. **4w** was obtained as an orange solid in mixture with MeLi (approx. 6 equiv of MeLi per W complex). Approximate yield deduced from NMR was 47% (0.044 g, 0.050 mmol). **^1H -RMN** (400 MHz, $[\text{D}_8]\text{THF}$) δ = 2.12–1.91 (quint, J = 7.1 Hz, 8H, PCH_2), 1.34–1.24 (m, 8H, CH_2), 1.11–1.04 (m, 12H, CH_3), 1.04–0.96 (m, 12H, CH_3), –2.25 (quint, $^3J_{\text{HP}}$ = 7.2 Hz, 3H, WCH_3). A signal for 8 CH_2 protons overlaps with the signals for THF and $[\text{D}_8]\text{THF}$. **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100 MHz, $[\text{D}_8]\text{THF}$) δ = 26.8 (quint, J_{CP} = 9.1 Hz, 4C, PCH_2), 21.6 (dt, J_{CP} = 22.1, 3.0 Hz, 4C, PCH_2CH_3), 10.3 (4C, CH_3), 9.9 (4C, CH_3), –21.8 (quint, $^2J_{\text{CP}}$ = 6.9 Hz, WCH_3). **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (162 MHz, $[\text{D}_8]\text{THF}$) δ = 37.4 (J_{PW} = 303 Hz). **IR (ATR)** $\nu_{\text{N-N}}$ = 1733 cm^{-1} (s).

***trans*-[MeMo(PMe $_2$ Ph) $_4\text{N}_2$ Li(THF) $_3$ (7Mo):** To a stirred solution of **3Mo** (0.062 g, 0.088 mmol) in THF (1.5 mL) in a screw-cap 10-mL Schlenk tube, an ether solution of MeLi (1.6 M, 60 μL , 0.10 mmol, 1.1 equiv) was added dropwise and the obtained green mixture was stirred in the dark at room temperature for 5 h under a nitrogen atmosphere. Pentane (15 mL) was added and the resulting mixture was stored at –40 °C for 1 h which caused the precipitation of a light-sensitive red solid. This solid was washed with pentane (2 \times 2 mL) and then the solvent was removed under reduced pressure during 10 min. A 76:24 mixture of **7Mo**/**8Mo** was obtained in 72 % yield (0.056 g, 0.063 mmol Mo). **^1H -RMN** (600 MHz, $[\text{D}_8]\text{THF}$) δ = 7.64–7.57 (m, 8H, H_{meta}); 7.04–6.94 (m, 12H, H_{ortho} + H_{para}), 1.35 (s, 24H, CH_3), –1.34 (quint, $^3J_{\text{HP}}$ = 6.6 Hz, 3H, MoCH_3). **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100 MHz, $[\text{D}_8]\text{THF}$) δ = 151.6 – 151.4 (m, 4 C_{ipso}), 132.0 – 131.8 (m, 8 C_{meta}), 127.3 – 127.2 (m, 8 C_{ortho}), 126.6 (8 C_{para}) 20.6 – 20.3 (m, 8C, PCH_3), –8.0 (quint, $^2J_{\text{CP}}$ = 9.1 Hz, MoCH_3). **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (243 MHz, $[\text{D}_8]\text{THF}$) δ = 10.9. **IR (ATR)** $\nu_{\text{N-N}}$ = 1740 cm^{-1} (s).

***trans*-[MeW(PMe $_2$ Ph) $_4\text{N}_2$ Li(THF) $_n$ (7w):** To a solution of **3w** (0.051 g, 0.064 mmol) in $[\text{D}_8]\text{THF}$ (0.7 mL) in a Young NMR tube, an ether solution of MeLi (4.6 M, 80 μL , 6.0 equiv) was added dropwise and the obtained orange mixture was stirred under irradiation at 460 nm for 3 h under an argon atmosphere. In a glove box, the solution was transferred to a 20-mL screw-cap tube (1 mL of THF was used to rinse the NMR tube) and pentane (15 mL) was added and the resulting mixture was stored at –40 °C for 1 h which caused the precipitation of a brown solid. This solid was washed with pentane (2 \times 2 mL) and then the solvent was removed under reduced pressure during 10 min. NMR analysis of this solid revealed a mixture of several compounds in which **7w** was the major component but partly degraded into an unidentified methyl complex. **^1H -RMN** (400 MHz, $[\text{D}_8]\text{THF}$) δ = 7.60–7.56 (m, 8H, H_{meta}); 7.02–6.97 (q, 12H, H_{ortho} + H_{para}) 1.46 (s, 24H, CH_3), –1.34 (quint, $^3J_{\text{HP}}$ = 7.3 Hz, 3H, WCH_3). **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100 MHz, $[\text{D}_8]\text{THF}$) δ = 151.5–151.7 (m, C_{IV}), 132.2 – 131.0 (m, 8 C_{meta}), 127.3 (s, 8 C_{ortho}), 126.8 (s, 4 C_{para}), 20.6 – 20.3 (m, PCH_3), –12.2 (quint, $^2J_{\text{CP}}$ = 9.1 Hz, WCH_3). **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (162 MHz, $[\text{D}_8]\text{THF}$) δ = –20.9 (J_{PW} = 307 Hz).

***fac*-[(PMe $_2$ Ph) $_3\text{MoMe}(\text{N}_2)_2\text{Li(THF)}_3$ (8Mo):** this compound was obtained as the minor component of a mixture with **7Mo** and could only be partially characterized. Its structure is tentative. **^1H -RMN** (600 MHz, $[\text{D}_8]\text{THF}$) δ = 7.47 – 7.41 (m, 3 H_{Ar}), 7.32 – 7.28 (m, 1 H_{Ar} , under a signal of free PMe $_2$ Ph), 7.15 (t, J = 7.4 Hz, 5 H_{Ar}), 7.06 (t, J = 7.5 Hz, 3 H_{Ar}), 1.46 (t, $^2J_{\text{HP}}$ = 2.3 Hz, 6H, $\text{P}(\text{CH}_3)_2$), 1.37 (t, $^2J_{\text{HP}}$ = 2.1 Hz, 6H, $\text{P}(\text{CH}_3)_2$), 1.06 (d, $^2J_{\text{HP}}$ = 4.8 Hz, 6H, $\text{P}(\text{CH}_3)_2$), –1.43 (dt, $^3J_{\text{HP}}$ = 6.7, 6.7 Hz, 3H, MoCH_3). The signals for 3 aromatic protons probably overlap with those of **7Mo**. **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100

MHz, $[\text{D}_8]\text{THF}$) δ = 148.8 (d, $^1J_{\text{CP}}$ = 18.1 Hz, C_{ipso}), 146.8 (t, $^1J_{\text{CP}}$ = 8.0 Hz, C_{ipso}), 130.9 (d, J_{CP} = 2.1 Hz, C_{Ar}), 130.8 (d, J_{CP} = 3.2 Hz, C_{Ar}), 127.6 (t, J_{CP} = 3.3 Hz, C_{Ar}), 19.2 (dt, $^2J_{\text{CP}}$ = 14.6, 2.7 Hz, $\text{P}(\text{CH}_3)_2$), 15.4 (td, $^2J_{\text{CP}}$ = 7.1, 1.3 Hz, $\text{P}(\text{CH}_3)_2$), 14.7 (t, $^2J_{\text{CP}}$ = 6.5 Hz, $\text{P}(\text{CH}_3)_2$). **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (243 MHz, $[\text{D}_8]\text{THF}$) δ = 12.0 (d, J_{PP} = 20.2 Hz), 11.1 (dd, J_{PP} = 21.1, 19.2 Hz).

$[\kappa^2\text{-(PMe}_2\text{C}_6\text{H}_4)\text{W(PMe}_2\text{Ph)}_3\text{N}_2\text{Li(THF)}_3$ (9w): In glove box, a 10-mL Schlenk tube was charged with **3w** (0.050 g, 0.063 mmol), which was then dissolved in $[\text{D}_8]\text{THF}$ (0.5 mL). The Schlenk tube was then capped with a septum and brought outside of the glove box. An ether solution of MeLi (1.6 M, 0.04 mL, 0.064 mmol, 1 equiv) was added dropwise and the orange solution was stirred at 60 °C for 24 h under N_2 . After cooling, the solution was transferred via canula to a Young NMR tube. NMR analysis revealed a mixture of free PMe $_2$ Ph and **9w** as major component and free PMe $_3$ and other minor unidentified diamagnetic W compounds as side products. Upon storing at –40 °C, one of our reaction mixture gave crystals of **9w** in low yield (0.005 g, 0.005 mmol, 8%). Attempts to obtain higher amounts of **9w** for further characterization failed. **$^{31}\text{P}\{^1\text{H}\}$ -NMR** (243 MHz, $[\text{D}_8]\text{THF}$) δ = –10.5 (d, $^2J_{\text{PP}}$ = 17.6 Hz, J_{PW} = 325.5 Hz, 1P), –12.1 (d, $^2J_{\text{PP}}$ = 14.1 Hz, J_{PW} = 307 Hz, 2P), –80.4 (dt, J_{PP} = 8.1, 14.6 Hz, 1P).

Acknowledgments

A. B. and A. S. acknowledge the European Research Council (ERC) for funding (Grant Agreement 757501). All authors are indebted to the French National Center for Scientific Research (CNRS) for financial support. We thank Drs. O. Baslé and D. Valyaev at LCC for lending us a photochemical apparatus.

Keywords: dinitrogen • methyllithium • molybdenum • tungsten • phosphines

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