Carborane Stabilized “19-Electron” Molybdenum Metalloradical

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ABSTRACT: Paramagnetic metal complexes gained a lot of attention due to their participation in a number of important chemical reactions. In most cases, these complexes are dominated by 17-e metalloradicals that are associatively activated with highly reactive paramagnetic 19-e species. Molybdenum paramagnetic complexes are among the most investigated ones. While some examples of persistent 17-e Mo-centered radicals have been reported, in contrast, 19-e Mo-centered radicals are illusive species and as such rarely be detected. In this work, the photodissociation of the \([\text{Cp}(\text{CO})_3\text{Mo}]_2\) dimer (1) in the presence of phosphines was revisited. As a result, the first persistent, formally 19-e Mo radical with significant electron density on the Mo center (22%), \(\text{Cp}(\text{CO})_2\text{Mo}^+\phi\text{PPH}_2(\phi-C_6\text{B}_{10}\text{H}_{11})\) (5b), was generated and characterized by EPR spectroscopy and MS as well as studied by DFT calculations. The stabilization of 5b was likely achieved due to a unique electron-withdrawing effect of the \(\phi\)-carboranyl substituent at the phosphorus center.

INTRODUCTION

Organometallic chemistry is mostly dominated by diamagnetic complexes, which obey the 16- and 18-electron rule.\(^1\)\(^2\) This rule is very useful for predicting the stability and reactivity of diamagnetic metal complexes. Since the 1980s, however, paramagnetic metal complexes began to gain significant attention due to their important role in a variety of chemical reactions.\(^3\)\(^7\) For instance, paramagnetic metal intermediates of the second and third rows are involved in redox reactions, chain mechanisms, homolytic cleavage, and catalysis of C–C bond formation\(^3\)\(^6\) as well as in mediating redox reactions in energy-conversion processes and in biomimetic C–H bond activation and epoxidation of hydrocarbons.\(^9\) Their intermediacy in industrial processes such as the Wacker reaction is also well-known.\(^10\) As a result, the range of organometallic chemistry has expanded to include numerous paramagnetic 17-e complexes, which exist as both stable complexes and short-lived intermediates.\(^3\)\(^4\)\(^6\)\(^8\)\(^11\)\(^12\) The reactions of paramagnetic 17-e metal complexes are associatively activated with 19-e intermediates or transition states.\(^3\)\(^4\)\(^11\) However, unlike 17-e metal complexes, 19-e metal complexes in which the unpaired electron is primarily metal localized in a M–L antibonding orbital are rare and usually and unstable and as such were proposed mostly as illusive intermediates.\(^4\)\(^12\)\(^13\) The 19-e Mo-centered radicals, to the best of our knowledge, have never been observed in chemical reactions, with the exception of femtosecond IR spectroscopy.\(^14\)\(^15\) Noteworthy, persistent 19-e Mo-centered radicals that are perhaps better described as 18-e complexes with reduced ligands (so-called “18 + \(\delta\)” complexes) were synthesized previously; however, the spin density on the metal center in these complexes was negligible (<1%).\(^16\)\(^19\)

One of the earliest reactions postulated to involve a 19-e intermediate was the photochemical disproportionation of the \([\text{Cp}(\text{CO})_3\text{Mo}]_2\) dimer (1) in the presence of \(\text{R}_3\text{P}\) into the \(\text{Cp}(\text{CO})_2\text{Mo}^+\phi\text{PPH}_2(\phi-C_6\text{B}_{10}\text{H}_{11})\) (5) and \(\text{Cp}(\text{CO})_3\text{R}_3\text{P}\) (3) ion pair (Scheme 1).\(^13\)\(^15\) The accepted mechanism for this reaction, proposed by Tyler and co-workers,\(^13\) proceeds through photoexcitation of 1 leading to Mo–Mo bond cleavage and the formation of two 17-e \(\text{Cp}(\text{CO})_3\text{Mo}^+\) radicals (4). In the presence of \(\text{R}_3\text{P}\) the formation of a highly reducing, transient 19-e intermediate \(\text{Cp}(\text{CO})_3(\text{R}_3\text{P})\text{Mo}^+\) (5) is proposed. Electron transfer from 5 to 4 leads to formation of \(\text{Cp}(\text{CO})_3(\text{R}_3\text{P})\text{Mo}^+\) (3) and \(\text{Cp}(\text{CO})_3\text{Mo}^+\) (2) (Scheme 1). Importantly, it was also shown that this reaction is reversible, and in the dark, this salt over time is converted back to 1 and \(\text{R}_3\text{P}\), either via a single electron transfer (SET) path (Scheme 1a) or directly by substitution of \(\text{R}_3\text{P}\) (Scheme 1b) with no clear indication as to which mechanism prevails in this transformation.\(^13\)\(^20\)

Noteworthy, when 1 was irradiated in the presence of a bidentate diphenphosphino-based ligand (2,3-bis(diphenylphosphino)maleic anhydride)), a stable isolable 18 + \(\delta\)
complex was formed with most of the spin density located at the diphosphine ligand (i.e., $\delta$ was close to zero). On the other hand, when $R_3P$ in this reaction (Scheme 1) was replaced by an N-heterocyclic carbene (NHC), a persistent 17-e $\text{Cp(CO)}_3\text{Mo}^-$ radical was formed via substitution of one of the COs by the carbene. Noteworthy, neither 17-e 4 nor 19-e 5 was observed or characterized by electron paramagnetic resonance (EPR) spectroscopy. We, therefore, decided to revisit this reaction (Scheme 1) and see whether radicals of type 5 could be stabilized in this process and studied by EPR spectroscopy. Herein, we report the generation and characterization of the first persistent formally 19-e Mo-based radical with a significant spin density of 22% on the Mo center, $\text{Cp(CO)}_3\text{Mo}^-$.

## RESULTS AND DISCUSSION

We first studied the photochemical reaction of 1 in the presence of $\text{Ph}_3P$. Thus, when a toluene solution containing 1 and $\text{Ph}_3P$ (1:10) in the EPR cavity was UV-irradiated ($\lambda > 300$ nm) at low temperature (200 K), a strongly low-field shifted singlet with a $g$-value of 2.082 was measured (Figure 1a), which immediately disappeared when irradiation was stopped. We assumed that this signal corresponded to the transient 17-e $\text{Cp(CO)}_3\text{Mo}^*$ radical (4) (Scheme 2a). To support our suggestion, 4 was optimized by using DFT (density functional theory), and its EPR parameters were calculated. The calculated $g$-value of 4 ($g = 2.069$) is in good agreement with the experimentally observed $g$-value (Figure 1b). To the best of our knowledge, this is the first time that the "parent" 17-e $\text{Cp(CO)}_3\text{Mo}^*$ radical (4) was experimentally observed by EPR spectroscopy.

After irradiation ($\lambda > 300$ nm) of the same toluene solution (1 and $\text{Ph}_3P$ (1:10)) at room temperature for 30 min, a high-intensity doublet was measured (14.2 G) with a $g$-value of 2.044 and a hyperfine coupling $a(95,97\text{Mo}) = 12.4$ G from magnetically active Mo isotopes (Figure 2a). This radical species was persistent with $\tau_{1/2} \approx 180$ min and thus allowed us to study its molecular composition using mass spectrometry (MS). Using atmospheric pressure chemical ionization (APCI) MS in positive mode, we were able to detect a mass that corresponds to a 17-e Mo-centered radical (647.9559 (M + H)$^+$) (Scheme 2b).

The computed EPR parameters in 6 are in good agreement with the experimental values considering the low spin density at the phosphorus.
center and rather complicated electronic structure of the Mo atom.24,25

We assumed that 6 was formed via unstable 19-e Mo-based intermediate 5a under irradiation (Scheme 2c). The unpaired electron in 5a can migrate to the σ* orbital at the phosphorus center under irradiation, giving the excited species 5a* (Scheme 2d).23,26 5a* resembles in its electronic structure phosphoranyl radicals (R₄P*), which tend to decay via α- or β-scission reactions,27–29 and thus 5a* decays in a similar manner via α-scission of the Ph–P bond, giving 18-e Cp(CO)₃MoPPh₂ (7) (Scheme 2e).30 7 may then substitute one of the CO groups at 4 to give 6 (Scheme 2f). A similar type of photoinduced CO substitution was previously reported.13,21

To overcome the problem of instability of 5a, especially under irradiation (see Scheme 2d,e), we decided to replace Ph₂P by Ph₃P(o-C₅H₄(C)₆F₁₁) (8) (Scheme 3).31,32 We envisioned that this substitution will solve a few of the problems that we encountered when using Ph₃P (Scheme 2). First, Ph₃P(o-C₅H₄(C)₆F₁₁) (8) is a weaker donor due to the strong electron-withdrawing effect of the o-carboranyl group33–35 and thus will lead to a less electron-rich Mo center, which would make the desired 19-e complex less reducing and as a result more stable.40 Second, the o-carboranyl substituent at the phosphorus center could help overcome the instability of 5a under irradiation. In contrast to 5a, which under irradiation is excited to a phosphoranyl-type radical 5a*, which decays via α-scission reaction (see Scheme 2d,e), in 5b the photoinduced electron migration would most probably lead to the migration of the spin density into the o-carboranyl cage, an effect that was previously shown by our and other groups.31–45 This may prevent the decay of 5b radical by α-scission (Scheme 2e).

The reaction between 1 and 8 (1:10) in toluene under UV irradiation (λ > 300 nm, 30 min) did not produce the desired radicals. However, when the solvent was changed to CH₂Cl₂,22 and the solution of 1 and 8 (1:2) was irradiated with visible light from a 34 W blue LED lamp (λ = 420–540 nm) for 1 h,46 the desired radical 5b was generated (Scheme 3) and was stable enough to study by EPR spectroscopy and MS methods (Figure 3).

The EPR spectrum of 5b (g = 1.980) is characterized by the hfcc with the 3¹P nucleus α(3¹P) = 21.3 G and magnetically active Mo isotopes (95,97Mo)α = 23.4 G (Figure 3a). The geometry of 5b was DFT optimized, and its EPR parameters were calculated.23 The calculated g-value (1.990) is in good agreement with the experimental g-value (1.980), with an hfcc of α(3¹P) = 10.8 G and α(95,97Mo)α = 23.4 G. The spin density is distributed between Mo (22%) and carbon atoms of the CO and C₅ groups (15–18%, for each carbon) (Figure 3c).23 Noteworthy, the spin density on the phosphine ligand (8) is negligible (2.4%).53 The mass corresponding to radical 5b (573.1174 (M–H)⁺) was found in the MS of the reaction mixture by using APCI MS in negative mode (Figure 3b). Noteworthy in 5b, the lower spin density on the Mo center (22%), as well as the negatively shifted g-value compared to a free electron (Δg = −0.0223), clearly contrasts with the higher spin density and positively shifted Δg of the 17-e Mo-centered radicals 2 (80%, Δg = 0.0797) and 6 (85%, Δg = 0.0417) (Schemes 1 and 2).

To the best of our knowledge, this is the first time that a persistent formally 19-e Mo-based radical complex with significant electron density on Mo (22%) was generated and studied spectroscopically. In contrast, doing the reaction between 1 and Ph₃P (1:2) under the same reaction conditions did not yield the 19-e Mo-based radical 5a, but radical 6 was observed by EPR spectroscopy (Scheme 2), meaning that the o-carboranyl substituent at the P center indeed plays a crucial role in stabilizing this type of radical.

Expectedly, in the dark, 5b was not stable over long periods of time (τ₁/₂ ≈ 48 h), and after a few days only the starting materials, 1 and 8, were detectable by NMR spectroscopy. Notably, when the same reaction mixture was irradiated again (λ = 420–540 nm), 5b was regenerated. Similar to the described reaction in Scheme 1, we assume that 5b is a persistent 19-e Mo radical intermediate of the dissociation reaction of 1 in the presence of 8.5,20 Interestingly, 5b extracted by pentane is more stable than in CH₂Cl₂ solution with τ₁/₂ ≈ 100 h.

Oxidation of 5b was achieved by its reaction with [Ph₃C][B(C₆F₅)₄], giving the corresponding cation [Cp(CO)₃(Ph₃P(o-C₅H₄(C)₆F₁₁))Mo⁺] (3b) (Scheme 3a), which...
was also independently synthesized, isolated, and fully characterized (X-ray molecular structure shown in Figure 4a). Noteworthy, 3b was also observed by $^{31}$P NMR (see Scheme 4). Formation of 5b in this process by EPR spectroscopy, suggesting that a rapid 2e reduction process dominates this transformation. This also suggests that the $E_{\text{peak}}^{\text{red(1)}}$ peak in the CV is a 2e event. Importantly, similar 2e reduction processes were reported previously. Because no paramagnetic species were observed at all stages of this experiment (Scheme 4), we assume that the reaction of 3b and 2 most likely proceeds via a closed-shell pathway and not through radicals 5b and 4 (Scheme 1).

**CONCLUSION**

To conclude, we work the photodissociation of 1 in the presence of Ph$_3$P and 8 was performed, and thorough EPR studies were done. The photochemical reaction of 1 with Ph$_3$P in toluene led to the formation of the persistent 17-e Mo-centered radical complex 6 via a transient “parent” 17-e complex Cp(CO)$_2$MoPh$_2$ (4), which was detected by EPR for the first time. 6 is presumably formed under irradiation which induces $\alpha$-scission reaction of a P–Ph bond, followed by adduct formation with 4. To overcome this problem, 8 was used instead of Ph$_3$P, which in reaction with 1 in CH$_2$Cl$_2$ under irradiation at $\lambda = 420–540$ nm gave the persistent formally 19-e Mo-based radical 5b. Accessing what previously had only been a hypothesized intermediate in Mo chemistry allowed us to carry out some preliminary reactivity studies. Oxidation of 5b by [Ph$_3$C][B(C$_6$F$_5$)$_4$] gave the corresponding cation 3b. The reaction of 5b with alkyl chlorides gave 9 via $\alpha$-atom abstraction and decarboxylation. The electrochemical reduction of 3b proceeds via two irreversible reduction events. To study this reduction process, 3b was reacted with FeCp$_2$, which via the 2e reduction process gave intermediate anion 2, which further led to dimer 1 and free 8; no paramagnetic species were observed in this process. We continue to study the chemistry of 5b and still search for its isolable analogues.

**EXPERIMENTAL SECTION**

**General Considerations.** All preparations were performed under an anhydrous N$_2$ atmosphere by using standard Schlenk and glovebox techniques (Vac.-Atmospheres Nexus II equipped with a $-35$ °C freezer). Toluene, dichloromethane, and hexane were dried by using a Vac. Solvent purification system. o-Diﬂuorobenzene and CDCl$_3$ were dried over CaH$_2$ for several days prior to distillation. All solvents were degassed by freeze–pump–thaw and stored on activated 4 Å molecular sieves prior to use. All glassware was oven-dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma-Aldrich, Strem, or Apollo Scientific and used without further purification unless indicated otherwise.
Spectroscopic Analyses. NMR spectra were recorded at room temperature by using a Bruker AvanceIII-400 MHz spectrometer and referenced to residual solvent, or externally (19F: BF₃·Et₂O; 18F: CFCl₃; 31P: 85% H₃PO₄) in some of the cases the tubes were equipped with DMSO-d₆ capillary as external standard. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constant (Hz). The EPR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.3 GHz) digital EPR spectrometer equipped with a Bruker T2 temperature controller. The spectra were recorded at a microwave power of 100—200 mW and a 100 kHz magnetic field modulation of 0.1—3.0 G amplitude (unless otherwise specified). The digital field resolution was 2048 points per spectrum. This allowed all hyperfine splittings to be measured directly with accuracy better than 0.1 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia software. When the reactions were performed under UV irradiation, a high-pressure mercury lamp (1000 W) (ARC lamp power supply model 69920) was used, with the output being focused on the sample with a quartz lens. When the reactions were performed under visible light irradiation (λ = 420—540 nm), a blue LED lamp (34 W) (Kessil, Model No. H150-BLUE) was used.

Electrochemical Measurements. The cyclic voltammetry (CV) measurements were performed by using a CHI760E electrochemical workstation. A 3 mm glassy carbon was used as the working electrode, Ag wire was used as the reference electrode and a Pt wire was used as the counter electrode. [nBu₄N][B(C₆F₅)₄] in CH₂Cl₂ (0.1 M) was used as a supporting electrolyte. All electrochemical measurements were performed under inert atmosphere in a glovebox. All the electrodes were rinsed with the electrolyte solution prior to use. For all CVs measurements, the first scan cycle was discarded.

X-ray Crystallography. Data were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (λ = 0.71073 Å). The crystals were mounted on a cryoloop with Paratone oil, and all data were collected at 100(2) K. Crystal structures were solved by direct methods and refined by full matrix least-squares. All hydrogen atom positions were idealized and rode on the atom of the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed by using a SHELXTL-2014 and a SHELXL-2014.

Synthesis of Cp(CO)₅MoPPh₂(o-C₆H₄(C₆H₅)₅) (5b). Inside the glovebox a Young NMR tube was charged with [Cp(CO)₅Mo]₂ (1) (0.05 g, 0.10 mmol) and Ph₂P(o-C₆H₄(C₆H₅)₅) (0.07 g, 0.20 mmol), 31P NMR (162 MHz; CDCl₃) δ 138.74 (t, J_C,P = 11.5 Hz, Ph), 136.81 (b, F,C = 13.5 Hz, Ph), 136.30 (b, F,C = 13.5 Hz, Ph), 135.37 (t, J_F,C = 10.9 Hz, Ph), 133.84 (b, Ph), 133.47 (b, C,F₃), 133.18 (t, J_F,C = 13.5 Hz, C,F₃), 132.61 (b, C,F₃), 131.38 (t, J_F,C = 13.5 Hz, C,F₃), 125.29 (t, J_F,C = 13.5 Hz, C,F₃), 124.65 (b, Ph), 124.68 (b, Ph), 122.75, 122.49 (CO). ¹H NMR (162 MHz; CDCl₃, 0.05 g, 0.10 mmol) and Ph₂P(o-C₆H₄(C₆H₅)₅) (0.20 g, 0.50 mmol) were added to a stirring solution at 70 °C followed by 1 h reaction. A freshly prepared CpMo(CO)₃H (0.25 g, 1.00 mmol) dissolved in 10 mL of chlorobenzene, DMSO-d₆ capillary) δ 6.98—7.08 (10H, m). ¹C NMR (100 MHz; CDCl₃, 1.28 mL, 6.93 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution. This dark violet solution, 8 (0.33 g, 1.00 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution. This dark violet solution, 8 (0.33 g, 1.00 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution. This dark violet solution, 8 (0.33 g, 1.00 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution. This dark violet solution, 8 (0.33 g, 1.00 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution. This dark violet solution, 8 (0.33 g, 1.00 mmol) dissolved in 5 mL of CH₂Cl₂ was added dropwise. The solution was allowed to stir for another hour, forming a dark violet solution.

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c03568.
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