

## Communications to the Editor

### [Mo<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-PPh<sub>2</sub>)(CO)<sub>4</sub>], a Reactive 33-Electron Binuclear Radical

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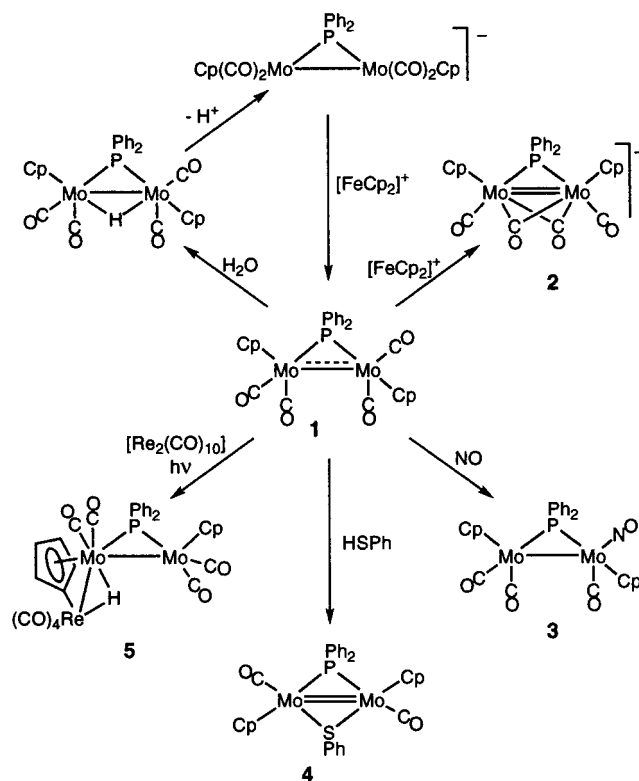
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The chemistry of metal-based radicals constitutes an area of considerable interest in the current organometallic research. This is mainly due to the fact that these species are involved as active intermediates or catalysts in many fundamental reactions such as ligand substitution, isomerization, atom transfer, electron transfer, or metal–metal bond formation.<sup>1</sup> Most of the studies in this area, however, have been devoted to the chemistry of mononuclear radicals. The behavior of related binuclear species in which two metal fragments are connected through bridging ligands having delocalized π-systems (polyaromatics, polypyridils, cumulenes, etc.) have also received considerable attention, mainly because of their physical properties.<sup>2</sup> In contrast, metal–metal-bonded binuclear radicals which have been detected or isolated so far are scarce, particularly those with electron counts below 34. The latter have been obtained typically upon electron-transfer reactions on suitable precursors, but little is known about the reactivity of these unsaturated molecules apart from their electrochemistry.<sup>1,3</sup> An exception to this is found for the 33-electron compounds [Fe<sub>2</sub>(μ-PPh<sub>2</sub>)(CO)<sub>7</sub>] and [CoTa(μ-CH<sub>2</sub>)<sub>2</sub>Cp<sub>3</sub>] (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) for which detailed studies on their rapid reactions toward phosphines<sup>4</sup> or organic disulfides<sup>5</sup> have been carried out, respectively.

In this paper we report the synthesis of the 33-electron, metal–metal-bonded radical [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PPh<sub>2</sub>)(CO)<sub>4</sub>] (**1**), which appears to be the first example of a neutral dimer having a M<sub>2</sub><sup>3+</sup> core (M = group 6 metal). More importantly, **1** is stable enough to be isolated and yet quite reactive toward a variety of reagents, so that its chemistry can be explored in detail (Scheme 1). In all of the reactions studied so far, the Mo<sub>2</sub> unit is preserved, thanks to the strongly bound diphenylphosphido bridge.

Compound **1** is rapidly formed upon oxidation of [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PPh<sub>2</sub>)(CO)<sub>4</sub>]<sup>-</sup> with 1 equiv of [FeCp<sub>2</sub>]<sup>+</sup>, and can be iso-

Scheme 1



lated as an air-sensitive green solid.<sup>6</sup> A further electron can be easily removed by [FeCp<sub>2</sub>]<sup>+</sup> to yield the doubly bonded cation [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PPh<sub>2</sub>)(μ-CO)<sub>2</sub>(CO)<sub>2</sub>]BF<sub>4</sub> (**2**) after some rearrangement of the carbonyl ligands.<sup>7</sup>

In solution, **1** reacts with different hydrogen sources (for example, water) to give the known hydrido derivative [Mo<sub>2</sub>Cp<sub>2</sub>(μ-H)(μ-PPh<sub>2</sub>)(CO)<sub>4</sub>].<sup>8</sup> The fact that the ν(CO) bands of the latter are similar to those of **1** suggests little structural reorganization upon H-atom transfer and hence an equal distribution of the odd electron on both metal fragments, in contrast to that found for the Fe<sub>2</sub> and CoTa radicals mentioned above. Further information on **1** has been obtained through ESR and CV studies.<sup>9</sup>

Compound **1** is very reactive toward traditional radical traps such as halogens or NO (5% in N<sub>2</sub>). In the latter reaction, decarbonylation also occurs rapidly even at 223 K to yield the tricarbonyl [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PPh<sub>2</sub>)(CO)<sub>3</sub>(NO)] (**3**)<sup>10</sup> the structure of which has been confirmed through an X-ray study.<sup>11</sup> For

(6) Selected spectroscopic data for **1**: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 1951 (w), 1905 (vs), 1879 (s) cm<sup>-1</sup>. All attempts to grow single crystals of this air-sensitive compound, suitable for an X-ray study, have been unsuccessful so far.

(7) Selected spectroscopic data for **2**: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2058 (vs), 2009 (s), 1763 (m, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 233 K) δ 5.37 (s, 10H, Cp). <sup>31</sup>P{<sup>1</sup>H} NMR (161.99 MHz) δ 119.9 (s).

(8) Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083–1088.

(9) The redox potentials for the couples anion/**1** and **1/2** were found to be -0.53 V and +0.08 V in dichloromethane solutions (vs the SCE electrode). Toluene solutions of **1** give rise to a single ESR resonance at 300 K (g = 2.048) which exhibits splitting (12 G) due to <sup>31</sup>P-coupling. Alvarez, C.; Connelly, N. G., unpublished results.

(10) Selected spectroscopic data for **3**: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 1944 (vs), 1898 (s), 1853 (m), ν(NO) 1637 (m) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (161.99 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 291 K) δ 193.2 (s).

(11) Bois, C., unpublished results.

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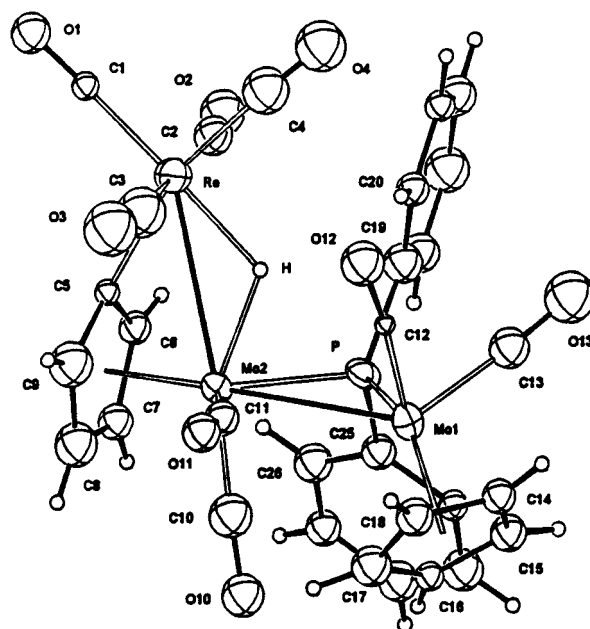
(5) Aubart, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, 118, 1793–1794.

comparison, we note that NO (5%) is unreactive at rt toward the electron precise  $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_4]$ .

Carbonyl displacement and atom-transfer processes occur in the reactions of **1** with secondary phosphines or thiols. Instead of H capture, hydrogen elimination occurs to give bis-phosphido or phosphido-thiolates in good yield, i.e.,  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PPh}_2)(\mu\text{-SPh})(\text{CO})_2]$  (**4**) from **1** and HSPH.<sup>12</sup> Thus, the synthesis of a large number of unsaturated dimers with tunable electronic and steric characteristics can be envisaged.

A further potential use of **1** concerns the synthesis of heterometallic clusters. This is illustrated by the photochemical reaction of **1** and  $[\text{Re}_2(\text{CO})_{10}]$  which cleanly gives the hydrido-cyclopentadienylidene cluster  $[\text{Mo}_2\text{ReCp}(\mu\text{-C}_5\text{H}_4)(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_8]$  (**5**)<sup>13</sup> whose structure has been fully elucidated by an X-ray analysis (Figure 1).<sup>14</sup> The formation of **5** can be understood in terms of initial radical coupling of **1** and  $\text{Re}(\text{CO})_5$  followed by CO loss on the rhenium fragment and the oxidative addition of a C–H(Cp) bond to the unsaturated center thus generated.<sup>15</sup> This implies a cis disposition of H and C(C<sub>5</sub>H<sub>4</sub>) donor atoms around Re, as found in the crystal. The formation of **5** represents the first example of a C–H(Cp) bond addition occurring at a  $\text{Re}(\text{CO})_x$  fragment. Indeed, only one other example involving rhenium has been previously described, this occurring at the much more basic  $\text{ReCp}(\text{PMe}_3)_2$  moiety.<sup>16</sup>

In summary, we have shown that the 33-electron radical **1** exhibits a wide chemistry involving several processes characteristic of mononuclear organometallic radicals such as atom transfer, ligand displacement, or metal–metal bond formation. Further



**Figure 1.** View of the molecular structure of complex **5** together with the atomic numbering system. Selected bond distances (Å) and angles (deg): Mo1–Mo2 3.134(6), Mo2–Re 3.258(5), Mo1–P 2.404(14), Mo2–P 2.459(14), Re–C5 2.16(2), Re–H 2.0(4), Mo2–H 2.0(4); Re–Mo2–Mo1 107.7(1), Mo1–P–Mo 80.2(4), C5–Re–H 78(10).

studies to extend the chemistry and synthetic potential of this reactive complex are now in progress.

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**Supporting Information Available:** Experimental procedures for the preparation of new complexes and microanalytical data. Data collection, refinement details and listings of atomic coordinates, thermal parameters, bond lengths and bond angles for the X-ray study on complex **5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(12) Selected spectroscopic data for **4**:  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ): 1889 (w, sh), 1852 (vs)  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR (81.02 MHz,  $\text{CD}_2\text{Cl}_2$ , 291 K)  $\delta$  107.3(s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.33 MHz)  $\delta$  242.9, 239.0 ( $2 \times \text{d}$ ,  $J(\text{PC})$  14 Hz, CO), 90.9, 90.7 ( $2 \times \text{s}$ , Cp).

(13) Selected spectroscopic data for **5**:  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ): 2084 (w), 1984 (vs), 1949 (s), 1907 (m), 1868 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200.13 MHz,  $\text{CD}_2\text{Cl}_2$ , 291 K)  $\delta$  5.9, 5.8, 5.7, 5.3 ( $4 \times \text{m}$ ,  $4 \times \text{1H}$ , C<sub>5</sub>H<sub>4</sub>), 5.2 (s, 5H, Cp), –14.8 (d,  $J(\text{HP})$  22 Hz, 1H,  $\mu\text{-H}$ ).

(14) X-ray data: black crystals of **5**, monoclinic ( $P2_1/c$ ),  $a = 9.060(5)$  Å,  $b = 15.228(6)$  Å,  $c = 21.978(7)$  Å,  $\beta = 96.69(2)^\circ$ ,  $V = 3012(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_1 = 0.0385$ , GOF = 1.396.

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