Organometallics **2005,** *24,* 5503−5505

High-Yield Synthesis and Reactivity of Stable Diiron Complexes with Bent-Phosphinidene Bridges

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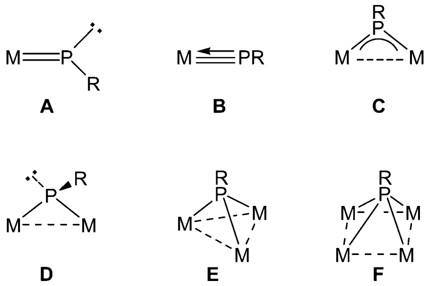
Received July 22, 2005

Summary: Reaction of [$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PRH_2)$] *(Cp* = $\eta^5\text{-}C_5H_5$*; R = Cy, Ph) with* [$FeCp_2$]BF_4 *gives the phosphide-bridged complexes* [$Fe_2Cp_2(\mu\text{-}PRH)(\mu\text{-}CO)(CO)_2$]$BF_4$*, which are deprotonated by M(OH) (M = Na, K) to give the phosphinidene derivatives* [$Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2$] *in high yield. The cyclohexylphosphinidene complex reacts at room temperature with MeI,* O_2*,* S_8*, or* $H_2C{=}CHR'$ *(R′ =* CO_2Me*) to give selectively* [$Fe_2Cp_2(\mu\text{-}PCyMe)(\mu\text{-}CO)(CO)_2$]*I or neutral derivatives of the types* [$Fe_2Cp_2\{\mu\text{-}P(E)Cy\}(\mu\text{-}CO)(CO)_2$] *(E = O, S) and* [$Fe_2Cp_2\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^1\text{-}CyPCH_2CHR'C(O)\}(\mu\text{-}CO)(CO)$]*.*

The chemistry of metal complexes having phosphinidene (PR) ligands is a subject of growing interest in the organometallic area. These versatile ligands can bind from one to four metal atoms in many different ways, some of them being the origin of high reactivity. This is especially so in the case of terminal complexes having bent PR ligands (**A** in Chart 1), in which the metal−phosphorus bond has considerable multiple-bond character and there is a lone pair at the phosphorus atom, all of which confers carbene-like reactivity to these complexes, thus enabling them to act as useful synthetic reagents in organophosphorus chemistry.[1]

In contrast, the chemistry of phosphinidene-bridged complexes of type **C** or **D** (Chart 1) has been little explored, even when the presence of multiple M−P bonding (type **C**) or a lone pair at phosphorus (type **D**) should lead to useful reactivity. Recently we started a study aimed at exploring the chemical behavior of cyclopentadienyl molybdenum complexes of type **C** (with R = 2,4,6-$C_6H_2{}^tBu_3$) having metal−metal bonds of formal orders from 1 to 3. We thus discovered several unusual reactions of the bridging phosphinidene group such as intramolecular C−H and P−C cleavages, η coordination of the aryl group, and intermolecular insertion of 1-alkynes.[2] In an extension of this work, we sought to prepare new phosphinidene-bridged complexes involving other transition metals. In particular, we noticed that there were only a few diiron species previously described in the literature. Moreover, most of these species were either thermally unstable (such as the cyclopentadienyl complex [$Fe_2Cp_2(\mu\text{-}PPh)(CO)_4$])[3] or transient species generated from suitable precursors, such as [$Fe_2\{\mu\text{-}P(N^iPr_2)\}_2(CO)_6$],[4] [$Fe_2(\mu\text{-}P^tBu)(CO)_6$],[5] and [$Fe_3(\mu_2\text{-}PPh)(\mu_3\text{-}PPh)(CO)_9$]$^{n-}$ (n = 1, 2).[6] All of these circumstances impose significant restrictions upon the study of the chemical behavior of the mentioned complexes. Finally, there is just one previous example of an stable diiron phosphinidene complex, [$Fe_2\{\mu\text{-}P(OR)\}_2(CO)_6$], with R being the bulky aryl 4,2,6-$C_6H_2Me^tBu_2$,[7] but no reactivity appears to have been developed around that complex. In this paper we report a high-yield synthetic procedure for the new and stable diiron complexes [$Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2$] having bent phenyl- or cyclohexylphosphinidene bridges and a preliminary study of their chemical behavior, illustrative of their high nucleophilicity.

Chart 1



The above phosphinidene complexes can be prepared through a two-step procedure. First, dehydrogenation on the neutral phosphine complexes [$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PRH_2)$] (R = Cy (**1a**),[8] Ph (**1b**))[9] is induced by

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(1) Reviews: (a) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95. (b) Lammerstma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127. (c) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938. (d) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210*, 181. (e) Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 314. (f) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9. (g) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445. (h) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (i) Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406.

(2) (a) García, M. E.; Riera, V.; Ruiz, M. A.; Sáez, D.; Vaissermann, J.; Jeffery, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 14304. (b) García, M. E.; Riera, V.; Ruiz, M. A.; Sáez, D.; Hamidov, H.; Jeffery, J. C.; Riis-Johannessen, T. *J. Am. Chem. Soc.* **2003**, *125*, 13044.

(3) (a) Klasen, C.; Effinger, G.; Schmid, S.; Lorenz, I.-P. *Z. Naturs-forch., B* **1993**, *48*, 705. (b) Lorenz, I.-P.; Pohl, W.; Noeth, H.; Schmidt, M. *J. Organomet. Chem.* **1994**, *475*, 211.

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(6) (a) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066. (b) Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897.

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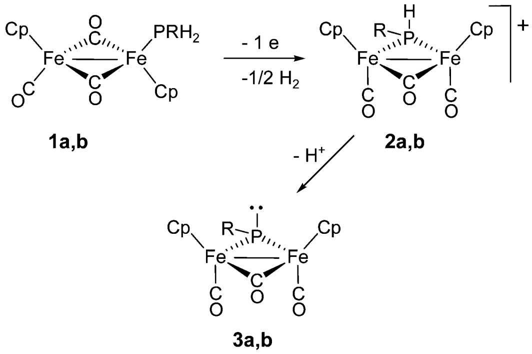
(8) Compounds **1a**,**b** were prepared as reported in ref 9 for the related complex [$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PHPh_2)$]. Selected spectroscopic data for **1a**: IR ν(CO) (CH_2Cl_2) 1935 (s), 1770 (w), 1730 (vs) cm^{-1}; ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 17.2 ppm; ^{1}H NMR ($CDCl_3$) δ 4.72 (s, 5H, Cp), 4.50 (d, J_{HP} = 1, 5H, Cp), 3.28 (dd, J_{HP} = 327, J_{HH} = 6, 2H, P−H) ppm.

10.1021/om050617v CCC: $30.25

Scheme 1



oxidation with $[FeCp_2]BF_4$ to give in high yield the cationic phosphide complexes $[Fe_2Cp_2(\mu\text{-}PRH)(\mu\text{-}CO)(CO)_2]BF_4$ (**2a**,**b**),[10] which display two terminal CO ligands almost parallel to each other (Scheme 1). To our knowledge this reaction constitutes a novel synthetic strategy for cationic phosphide-bridged complexes, and it seems quite general, since it can be applied to other diiron complexes having different primary or secondary phosphines, currently under study. We note that, during the course of this work, Sugiura et al. reported a medium-yield (based on the starting $[Fe_2Cp_2(CO)_4]$) preparation of the triflate salt of the cation present in **2b**.[11]

The second step in the preparation of the phosphinidene complexes **3** is a more conventional deprotonation of the remaining P−H bond, which can be quantitatively accomplished in dichloromethane solution using solid M(OH) (M = Na, K) or other strong bases. The presence of the phosphinidene ligand in complexes **3a**,**b** is denoted by their high ^{31}P chemical shifts[12,13] and has been further confirmed through an X-ray study on the phenylphosphinidene complex **3b** (Figure 1).[14] The phosphorus atom displays a pyramidal environment, with the phenyl group pointing away from the Cp ligands as expected on steric grounds, while the Fe−P and Fe−Fe lengths are consistent with the formulation of single bonds between these atoms, as proposed according to the EAN rule. We should note that complex **3b** is the first diiron compound having a bent-phosphinidene bridge to be structurally characterized.

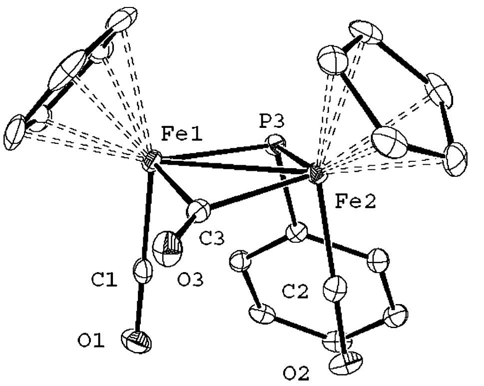
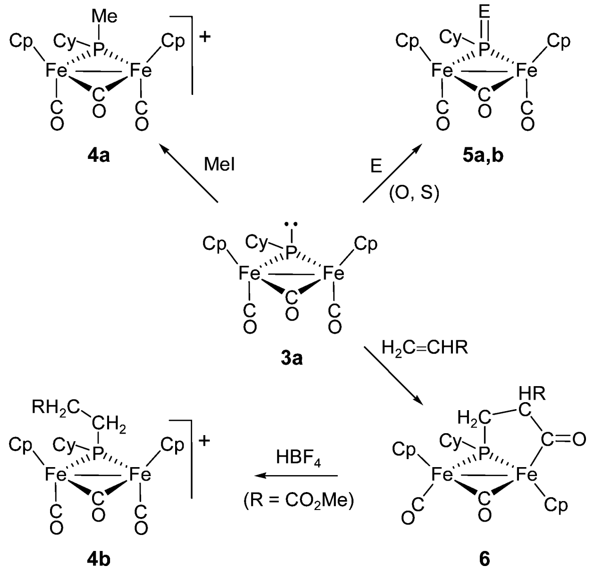


Figure 1. ORTEP diagram of compound **3b**, with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.5879(4), Fe(1)−C(1) = 1.756(2), Fe(2)−C(2) = 1.755(2), Fe(1)−C(3) = 1.922(2), Fe(2)−C(3) = 1.928(2), Fe(1)−P(3) = 2.2584(6), Fe(2)−P(3) = 2.2648(6); C(1)−Fe(1)−Fe(2) = 97.3(1), C(2)−Fe(2)−Fe(1) = 98.1(1), C(1)−Fe(1)−C(3) = 86.6(1), C(2)−Fe(2)−C(3) = 87.0(1), C(1)−Fe(1)−P(3) = 91.2(1), C(2)−Fe(2)−P(3) = 91.8(1), Fe(1)−P(3)−C(31) = 115.0(1), Fe(2)−P(3)−C(31) = 112.7(1)°.

Scheme 2



Both the presence of a lone pair at the phosphorus atom and the relatively good donor properties of the cyclopentadienyl ligands cause complexes **3** to be good nucleophiles, as illustrated by the reactions of the cyclohexyl derivative **3a** (Scheme 2). Thus, complex **3a** is reactive enough to achieve nucleophilic substitution on methyl iodide at room temperature to give the corresponding methylcyclohexylphosphide derivative $[Fe_2Cp_2(\mu\text{-}PCyMe)(\mu\text{-}CO)(CO)_2]I$ (**4a**),[15] thus paralleling the behavior of phosphinidene bridges at anionic metal centers,[16] or the electron-rich $[Pt_2(\mu\text{-}PMes)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[17] and $[Fe_2Cp_2(\mu\text{-}PPh)(CO)_4]$.[3]

Compound **3a** reacts rapidly at room temperature with air or elemental sulfur to give the corresponding derivatives $[Fe_2Cp_2\{\mu\text{-}P(E)Cy\}(\mu\text{-}CO)(CO)_2]$ (E = O (**5a**),[18] S (**5b**)[19]) having phosphinidene oxide or phosphinidene

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[9] Alvarez, C. M.; García, M. E.; Ruiz, M. A.; Connelly, N. G. *Organometallics* **2004**, *23*, 4750.

[10] Selected spectroscopic data for **2a**: IR ν(CO) (CH_2Cl_2) 2019 (vs), 1990 (w), 1833 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 223.4; ^1H NMR ($CDCl_3$) δ 8.13 (dd, J_{HP} = 390, J_{HH} = 10, 1H, P−H), 5.17 (s, 10H, Cp).

[11] Sugiura, J.; Kakizawa, T.; Hashimoto, H.; Tobita, H.; Ogino, H. *Organometallics* **2005**, *24*, 1099.

[12] Selected spectroscopic data for **3a**: IR ν(CO) (CH_2Cl_2) 1977 (vs), 1940 (w), 1773 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 531.6; ^1H NMR (C_6D_6) δ 4.24 (s, 10H, Cp).

[13] Selected spectroscopic data for **3b**: IR ν(CO) (CH_2Cl_2) 1988 (vs), 1952 (w), 1783 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 498.2; ^1H NMR (CD_2Cl_2) δ 4.90 (s, 10H, Cp).

[14] X-ray data for **3b**: dark brown crystals, monoclinic ($P2_1/n$), a = 7.9442(7) Å, b = 27.055(3) Å, c = 7.7879(7) Å, β = 95.843(2)°, V = 1665.1(3) $Å^3$, T = 173 K, Z = 4, R = 0.028 (observed data with $I > 2\sigma(I)$), GOF = 0.992.

[15] Selected spectroscopic data for **4a**: IR ν(CO) (CH_2Cl_2) 2015 (vs), 1985 (w), 1829 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 271.2; ^1H NMR (CD_2Cl_2) δ 5.37 (s, 10H, Cp), 2.93 (d, J_{HP} = 12, 3H, Me).

[16] (a) Deeming, A. J.; Doherty, S.; Day, M. W.; Hardcastle, K. I.; Minassian, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1273. (b) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145. (c) Haupt, H.-J.; Schwefer, M.; Egold, H.; Flörke, U. *Inorg. Chem.* **1995**, *34*, 5461. (d) Maslennikov, S. V.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2483.

[17] Kourkine, I. V.; Glueck, D. S. *Inorg. Chem.* **1997**, *36*, 5160.

[18] Selected spectroscopic data for **5a**: IR ν(CO) (CH_2Cl_2) 1985 (vs), 1951 (w), 1788 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 343.8; ^1H NMR ($CDCl_3$) δ 4.87 (s, 10H, Cp).

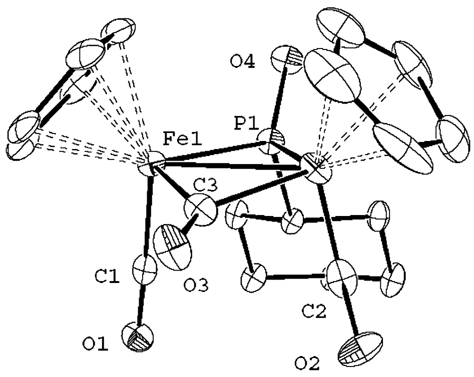

Figure 2. ORTEP diagram of compound **5a**, with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.601(2), Fe(1)−C(1) = 1.747(5), Fe(2)−C(2) = 1.748(5), Fe(1)−C(3) = 1.914(5), Fe(2)−C(3) = 1.926(4), Fe(1)−P(1) = 2.219(2), Fe(2)−P(1) = 2.216(2), P(1)−O(4) = 1.503(3); C(1)−Fe(1)−Fe(2) = 99.2(1), C(2)−Fe(2)−Fe(1) = 99.4(2), C(1)−Fe(1)−C(3) = 89.3(2), C(2)−Fe(2)−C(3) = 90.3(2), C(1)−Fe(1)−P(1) = 92.0(1), C(2)−Fe(2)−P(1) = 91.3(1), Fe(1)−P(1)−O(4) = 121.6(1), Fe(2)−P(1)−O(4) = 120.7(1)°.

sulfide ligands bridging the dimetal center exclusively through the P atom, as confirmed crystallographically for **5a** (Figure 2).[20] We have pointed out recently that the chemistry of the phosphinidene oxide ligand is largely unexplored at present.[21] In fact, only one other diiron complex having a P(O)R ligand has been previously described ([$Fe_2Cp_2\{\mu$-P(O)OH$\}(\mu$-CO)(CO)$_2$]).[22] On the other hand, precedents for diiron complexes having phosphinidene sulfide ligands are also scarce; they are in fact restricted to the phenyl derivatives [$Fe_2Cp_2\{\mu$-P(S)Ph$\}(CO)_n$] ($n = 3, 4$), both of which have no metal−metal bond.[23] The presence of the uncoordinated P═O and P═S functionalities in complexes **5** might allow further transformations at the phosphinidene bridge, currently under exploration.

The most remarkable observation concerning the chemical behavior of the phosphinidene complex **3a**, not paralleled by other complexes having bent-phosphinidene bridges, lies in its ability to react with alkynes or activated olefins under mild conditions. For example, **3a** reacts with methyl acrylate (CH_2CHCO_2Me) at room temperature or above to give the very air-sensitive derivative [$Fe_2Cp_2\{\mu$-κ^1:κ^1,η^1-CyPCH$_2$CHRC(O)$\}(\mu$-CO)(CO)] (**6**; R = CO_2Me) having a phosphide−acyl ligand resulting from coupling among the entering alkene, the phosphinidene group, and a carbonyl ligand.[24] Attempts to isolate compound **6** as a pure material have been unsuccessful so far. Interestingly, the phosphide−acyl ligand in **6** is easily protonated by $HBF_4 \cdot OEt_2$ to give the corresponding alkylcyclohexylphosphide derivative [$Fe_2Cp_2\{\mu$-P(CH$_2$CH$_2$R)Cy$\}(\mu$-CO)(CO)$_2$]BF_4 (**4b**),[25] which has the same structure as the methyl compound **4a**. The transformations **2a/3a/6/4b** complete the insertion of an olefin into the P−H bond of the phosphide complex **2a** through a deprotonation/reprotonation sequence involving a phosphinidene intermediate. This can be then considered as an alternative to the radical-chain mechanism recently proposed for the hydrophosphination of phenylacetylene and methyl acrylate by the cation present in **2b**.[11] As stated above, the phosphinidene complex **3a** reacts with other olefins and alkynes. The latter reactions are more complex and are currently under study in our laboratory.

In summary, we have shown that the phosphinidene complexes [$Fe_2Cp_2(\mu$-PR$)(\mu$-CO)(CO)$_2$] (R = Cy, Ph) can be prepared in high yield through a novel redox-induced dehydrogenation of coordinated PRH_2 ligands, followed by deprotonation of the resulting PRH-bridged cations. As illustrated through the reactions of the cyclohexylphosphinidene compound, these complexes are strong nucleophiles able to react selectively at room temperature with methyl iodide, oxygen, sulfur, or even some activated olefins such as methyl acrylate to give neutral or cationic derivatives of the type [$Fe_2Cp_2\{\mu$-P(E)Cy$\}(\mu$-CO)(CO)$_2$]$^{n+}$ ($n = 1$, E = Me; $n = 0$, E = O, S) and [$Fe_2Cp_2\{\mu$-κ^1:κ^1,η^1-CyPEC(O)$\}(\mu$-CO)(CO)] (E = CH_2CHCO_2Me), which in several cases are difficult to prepare otherwise. Our results suggest that binuclear complexes having bent-phosphinidene bridges might be operative in hydrophosphination of olefins and related reactions involving P−H bonds of bridging alkyl- or arylphosphide ligands.

Acknowledgment. We thank the MCYT of Spain for financial support (Project BQU2003-05471).

Supporting Information Available: Text giving experimental procedures and spectroscopic data for new compounds and CIF files giving crystallographic data for compounds **3b** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Selected spectroscopic data for **5b**: IR ν(CO) (CH_2Cl_2) 1989 (vs), 1957 (w), 1794 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 345.6; ^1H NMR ($CDCl_3$) δ 4.81 (s, 10H, Cp).

(20) X-ray data for **5a**: red crystals, monoclinic ($P2_1/c$), a = 8.084(7) Å, b = 12.317(11) Å, c = 18.743(16) Å, β = 100.78(1)°, V = 1833(3) Å^3, T = 293 K, Z = 4, R = 0.049 (observed data with $I > 2\sigma(I)$), GOF = 0.968.

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(23) Lorenz, I.-P.; Muerschel, P.; Pohl, W.; Kurt, P. *Chem. Ber.* **1995**, *128*, 413.

(24) Selected spectroscopic data for **6**: IR ν(CO) (CH_2Cl_2) 1951 (vs), 1785 (s), 1730 (m, CO_2Me), 1611 (m, C(O)Fe) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 296.5; ^1H NMR (CH_2Cl_2) δ 4.76, 4.60 (2 × s, 2 × 5H, Cp), 3.69 (s, 3H, OMe).

(25) Selected spectroscopic data for **4b**: IR ν(CO) (CH_2Cl_2) 2015 (vs), 1985 (w), 1830 (m), 1736 (m, CO_2Me) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 276.0; ^1H NMR (CD_2Cl_2) δ 5.27 (s, 10H, Cp), 3.82 (s, 3H, OMe), 3.40, 3.24 (2 × m, 2 × 2H, PCH_2CH_2).