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Chemical and Structural Effects of Bulkness on Bent-Phosphinidene Bridges: Synthesis and Reactivity of the Diiron Complex $[Fe_2Cp_2\{\mu\text{-}P(2,4,6\text{-}C_6H_2{}^tBu_3)\}(\mu\text{-}CO)(CO)_2]$

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Summary: The steric pressure introduced by the 2,4,6-$C_6H_2{}^tBu_3$ group (R) in the complex $[Fe_2Cp_2(\mu\text{-}PR^*)(\mu\text{-}CO)(CO)_2]$ (Cp = η^5-C_5H_5) has pronounced effects with regard to its synthesis, structure, thermal stability, and general reactivity of the bent phosphinidene bridge, enabling it, for instance, to react with hydrogen under mild conditions (ca. 4 atm, 290 K).*

It is well-known that steric effects have a pronounced influence not only on the structure but also on the stability and reactivity of chemical species in general, and examples of the consequences of introducing bulky groups in molecules can be found in all areas of chemistry. Within the realm of organometallic chemistry, for instance, we can quote the use of η^5-C_5Me_5 instead of η^5-C_5H_5 ligands or of phosphine ligands PR_3 having very bulky instead of “normal-sized” R groups. In this way, novel structures and novel reactivity can be found that would be otherwise impossible to reach. Recent outstanding achievements of this strategy are the use of very bulky aryl (Ar) or silyl (X) groups to build the first examples of stable quintuply bonded dimetal complexes (Cr_2Ar_2)[1] and of triply bonded disilicon species (Si_2X_2), respectively.[2]

Bulky substituents have been used also in the very active area of phosphinidene (PR) complexes,[3] mainly to stabilize mononuclear species,[3d,i,l,m] but also binuclear species.[4] Recently, we reported a high-yield synthetic procedure for the new diiron complexes $[Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2]$ (Cp = η^5-C_5H_5) having bent phenyl- or cyclohexylphosphinidene bridges.[5] These compounds are themselves stable at room temperature but are also highly reactive under mild conditions toward a great variety of electrophilic molecules ranging from simple alkyl halides or chalcogens to alkenes, alkynes, diazo compounds, and organic azides, to give in some cases novel or unexpected organophosphorus ligands coordinated at the diiron center.[5,6] It was thus of interest to examine the influence of steric effects in all this rich chemistry, which we have done by using a quite bulky aryl group (R* = 2,4,6-$C_6H_2{}^tBu_3$) as substituent in the phosphinidene ligand. In this communication we report the preparation and a preliminary study of the reactivity of the corresponding diiron complex $[Fe_2Cp_2(\mu\text{-}PR^*)(\mu\text{-}CO)(CO)_2]$ (**3**). As will be shown below, the increased steric demands of the R* group have pronounced effects at all levels, since significant differences (when compared to the complexes having PCy and PPh ligands) are found for compound **3** concerning its synthesis, structure, thermal stability, and general reactivity.

The mentioned phosphinidene complex can be prepared through a two-step procedure (Scheme 1). First, a double oxidation coupled to deprotonation is induced on the corresponding arylphosphine complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR^*H_2)]$ (**1**)[7] by reacting it with 2 equiv of $[FeCp_2]BF_4$ in the presence of $NaHCO_3$, to give with high yield the cationic phosphide-bridged complex $[Fe_2Cp_2(\mu\text{-}PR^*H)(\mu\text{-}CO)(CO)_2]BF_4$ (**2**),[8] which displays two terminal CO ligands almost parallel to each other, as observed for the PCy or PPh complexes. Here we find, however, the first important effect of the R* group, since the less bulky phosphide complexes are not formed via two-electron oxidation of their phosphine complexes, but just following a single-electron oxidation/dehydrogenation sequence.[5] Apparently, the radical complex emerging from the first oxidation step of **1** is stabilized by the bulky R* group enough to prevent its spontaneous dehydrogenation, a matter to be studied in detail in the future.

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(7) Compound **1** was prepared as reported in ref 5 for the related complexes $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PRH_2)]$ (R = Ph, Cy). Selected spectroscopic data for **1**: ν(CO) (CH_2Cl_2) 1936 (m), 1772 (w), 1732 (vs) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −21.3 ppm; ^1H NMR (CD_2Cl_2, *trans* isomer) δ 4.71 (s, 5H, Cp), 4.44 (d, J_{HP} = 343, 2H, P−H), 3.99 (s, 5H, Cp) ppm.

(8) Preparation of **2**: solid $[FeCp_2]BF_4$ (0.400 g, 1.467 mmol) was slowly added to a stirred suspension of $NaHCO_3$ (1.0 g, 11.9 mmol) in a dichloromethane solution (30 mL) of compound **1** (0.400 g, 0.662 mmol) at 243 K, and the mixture was further stirred for 2 h at the same temperature to give a red solution yielding compound **2** (0.420 g, 92%) after workup. Selected spectroscopic data: ν(CO) (CH_2Cl_2) 2028 (vs), 2000 (w), 1825 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 181.7 ppm; ^1H NMR (CD_2Cl_2) δ 9.88 (d, J_{HP} = 385, 1H, P−H), 5.32 (s, 10H, Cp) ppm.

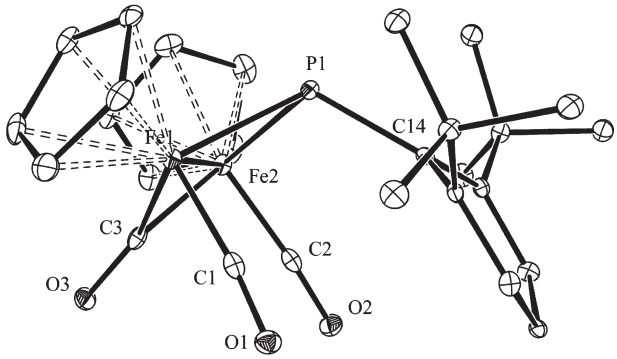
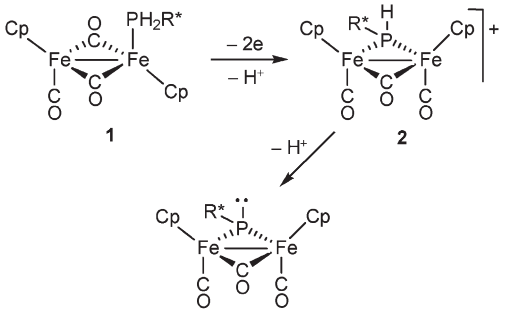
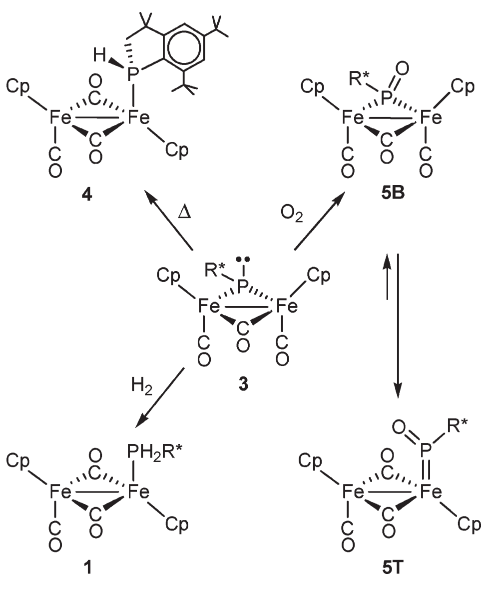


Figure 1. ORTEP diagram of compound **3**, with H atoms and the *p*-^{t}Bu group omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.5763(5), Fe(1)−C(1) = 1.758(3), Fe(2)−C(2) = 1.762(3), Fe(1)−C(3) = 1.911(3), Fe(2)−C(3) = 1.915(3), Fe(1)−P(1) = 2.305(1), Fe(2)−P(1) = 2.306(1), P(1)−C(14) = 1.893(2); C(1)−Fe(1)−Fe(2) = 100.8(1), C(2)−Fe(2)−Fe(1) = 98.1(1), C(1)−Fe(1)−C(3) = 85.6(1), C(2)−Fe(2)−C(3) = 86.4(1), C(1)−Fe(1)−P(1) = 94.3(1), C(2)−Fe(2)−P(1) = 94.0(1), Fe(1)−P(1)−Fe(2) = 67.9(1), Fe(1)−P(1)−C(14) = 113.5(1), Fe(2)−P(1)−C(14) = 113.2(1).

Scheme 1



Scheme 2



The second step in the preparation of the phosphinidene complex **3** is a more conventional deprotonation of the P−H bond remaining in the phosphide-bridged cation **2**, which can be quantitatively accomplished in dichloromethane solution using solid K(OH) and other strong bases. The presence of the phosphinidene ligand in **3** is denoted by the strong deshielding of its ^{31}P nucleus[9] and has been further confirmed through an X-ray study (Figure 1).[10] The structure is qualitatively similar to that of the corresponding phenylphosphinidene complex,[5] but there are significant quantitative differences concerning the bent (or pyramidal) phosphinidene ligand in **3**: (a) Fe−P and P−C(aryl) lengths ca. 0.05 Å longer, (b) a strong deviation of the aryl ring from planarity, to adopt an incipient boat conformation that takes the ortho ^{t}Bu groups away from the terminal cyclopentadienyl (H···H = ca. 2.2 Å) and carbonyl (H···C/O = ca. 2.6 Å) ligands, and (c) a slight bending of the terminal carbonyls away from the aryl group. All these effects can be considered as indicative of the presence of a severe steric crowding introduced by the bulky R* group in this complex. We also note that, although the boat deformation of the R* group has been previously found in other sterically overcrowded molecules,[11] that observed in **3** seems particularly large, as indicated by the tip angles for the ipso and para carbon atoms of the ring (ca. 22 and 10°, respectively).

The steric crowding in compound **3** is perhaps behind its low thermal stability. Indeed, this complex rearranges slowly (conversion ca. 80% after 4 day) in toluene solution at room temperature by undergoing intramolecular insertion of the P atom into a C−H bond of one of the close *o*-^{t}Bu groups (P···H = ca. 2.55 Å in the crystal), to give the phosphine derivative [$Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}$] (**4**),[12] the latter having a structure comparable to that of the phosphine complex **1** (Scheme 2). Expectedly, this transformation is much faster at higher temperatures, and it can be completed in ca. 1 h at 338 K in toluene solution. As found for **1**, complex **4** exists in solution as an equilibrium mixture of trans and cis isomers, these differing in the relative orientation of the Cp or (CO/phosphine) ligands, with the former being the major isomers, as is usually found for phosphine derivatives of the type [$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)$]. The C−H bond cleavage of the ^{t}Bu group in a PR* ligand to yield the free or metal-bound phosphine $PH(CH_2CMe_2)C_6H_4{}^tBu_2$ has been previously reported to occur on a few transient mononuclear complexes.[13]

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[9] Preparation of **3**: solid KOH (ca. 0.1 g, excess) was added to a dichloromethane solution (6 mL) of compound **2** (0.050 g, 0.072 mmol) at room temperature, and the mixture was vigorously stirred for 5 min to give a wine red solution which yielded compound **3** (0.042 g, 95%) after workup. Selected spectroscopic data: ν(CO) (CH_2Cl_2) 1991 (vs), 1958 (w), 1769 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 593.4 ppm; ^{1}H NMR (CD_2Cl_2) δ 4.86 (s, 10H, Cp) ppm.

[10] X-ray data for **3**: red crystals, triclinic ($P\bar{1}$), $a = 9.7459(4)$ Å, $b = 11.4820(5)$ Å, $c = 13.4931(6)$ Å, $\alpha = 73.027(2)°$, $\beta = 85.188(2)°$, $\gamma = 76.050(2)°$, $V = 1401.4(1)$ Å^3, $T = 100$ K, $Z = 2$, $R = 0.0358$ (observed data with $I > 2\sigma(I)$), GOF = 1.045.

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[12] Preparation of **4**: a toluene solution (5 mL) of compound **1** (0.050 g, 0.083 mmol) was placed in a Schlenk tube equipped with a Young valve, and it was stirred at 338 K for 1 h to give a brown-green mixture yielding compound **4** (0.036 g, 71%) after chromatographic separation. Selected spectroscopic data: ν(CO) (CH_2Cl_2) 1934 (m), 1772 (w), 1730 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 36.8 (trans), 37.5 (cis) ppm; ^{1}H NMR (C_6D_6, isomer trans) δ 4.56 (dd, $J_{HP} = 348$, $J_{HH} = 5$, 1H, P−H), 4.47, 4.09 (2s, 2 × 5H, Cp), 2.53, 1.99 (2 m, 2 × 1H, CH_2), 1.66, 1.00 (2s, 2 × 3H, Me) ppm.

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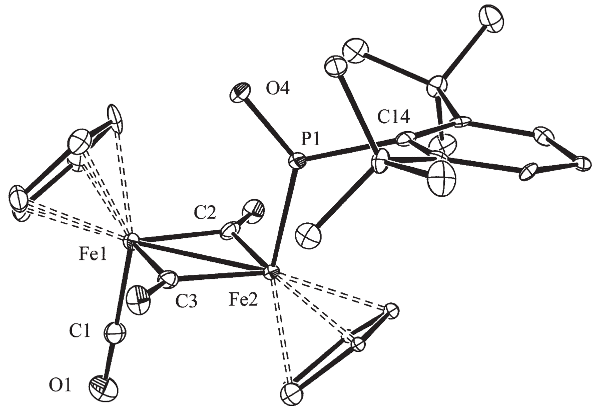

Figure 2. ORTEP diagram of compound *trans*-**5T**, with H atoms and the *p*-^{t}Bu group omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.556(1), Fe(1)−C(1) = 1.760(8), Fe(1)−C(2) = 1.910(7), Fe(1)−C(3) = 1.923(6), Fe(2)−C(2) = 1.936(7), Fe(2)−C(3) = 1.926(6), Fe(2)−P(1) = 2.091(2), P(1)−O(4) = 1.484(4), P(1)−C(14) = 1.840(7); C(1)−Fe(1)−Fe(2) = 96.2(2), C(1)−Fe(1)−C(2) = 94.6(3), C(1)−Fe(1)−C(3) = 96.3(3), P(1)−Fe(2)−C(2) = 97.6(2), P(1)−Fe(2)−C(3) = 90.4(2), P(1)−Fe(2)−Fe(1) = 98.1(1), Fe(2)−P(1)−O(4) = 129.5(2), Fe(2)−P(1)−C(14) = 118.6(2), O(4)−P(1)−C(14) = 111.6(3).

Interestingly, we recently proposed that the dimolybdenum complex [$Mo_2Cp_2(\mu$-PR*)$(CO)_4$], having a trigonal (four-electron-donor) PR* bridge, undergoes a related C−H bond cleavage reaction via a photoexcited state having a pyramidal (two-electron-donor) PR* bridge.[14] The observable transformation **3**/**4** thus provides indirect support for the above proposal.

The structural effects imposed by the bulky R* group on the reaction products arising from complex **3** are illustrated through its reaction with oxygen. The latter takes place rapidly at room temperature in the presence of air to give initially the oxophosphinidene-bridged derivative [$Fe_2Cp_2\{\mu$-P(O)R*$\}(\mu$-CO)$(CO)_2$] (**5B**),[15] thus resembling the behavior of the related PPh and PCy complexes.[5] However, this product slowly rearranges at room temperature to reach an equilibrium with its isomer [$Fe_2Cp_2(\mu$-CO$)_2$(CO)\{P(O)R*\}] (**5T**), the latter having a terminally bound oxophosphinidene ligand.[16] Compound **5T** is the major species in all solvents examined, and in turn it exists in solution as a mixture of the corresponding trans and cis isomers, as found for compounds **1** and **4** (see the Supporting Information). An X-ray study confirmed the structure of *trans*-**5T** (Figure 2).[17] In comparison to the geometrical parameters of the oxophosphinidene-bridged complex [$Fe_2Cp_2\{\mu$-P(O)Cy$\}(\mu$-CO)$(CO)_2$], we note that the terminal ligand in **5T** exhibits a similarly short P−O length of ca. 1.48 Å but a substantially shorter Fe−P length of ca. 2.10 Å. The latter figure can be compared to the value of ca. 2.22 Å for the mentioned diiron complex[5] or to values of ca. 2.13−2.21 Å for different phosphite and phosphine (L) complexes of the type [$Fe_2Cp_2(\mu$-CO$)_2$(CO)(L)].[18] All of the above data suggest the presence of substantial multiplicity in the Fe−P bond of **5T**, also consistent with the strong deshielding of its ^{31}P nucleus (δ_P ca. 433 ppm, to be compared to 312 ppm for the isomer **5B**). We should stress that compound **5** is the first Fe complex having a terminal oxophosphinidene ligand to be reported, with previous comparable species being restricted so far to Cr,[19a] Re,[19b] and Mo compounds.[20] Because of this paucity of suitable complexes, the chemistry of the phosphinidene oxide ligand remains largely unknown at present, and compound **5** thus offers an excellent opportunity to explore this chemistry at an iron center, currently under way.

Although the reactions discussed above are indeed singular in the context of the isolable phosphinidene complexes, the most remarkable observation concerning the chemical behavior of **3**, not paralleled by other phosphinidene complexes of any type, lies however in its ability to react with hydrogen under mild conditions. Thus, upon stirring a toluene solution of **3** under hydrogen (ca. 4 atm) at room temperature for ca. 20 h, a mixture containing the phosphine complex **1** as the major product is obtained, along with small amounts of free phosphine PR*H_2, the dimer [$Fe_2Cp_2(CO)_4$], and complex **4**. Most of the last complex is surely formed from the slow thermal rearrangement of **3** discussed above, while a separate experiment revealed that compound **1** in turn decomposes slowly in dichloromethane solution at room temperature to give free phosphine PR*H_2 and [$Fe_2Cp_2(CO)_4$] as major products. Thus, it seems that the hydrogenation of **3** is quite selective and gives mainly the phosphine complex **1** through a formal oxidative addition of the H−H bond to the lone-pair-bearing P atom. This is a remarkable reaction since, to our knowledge, no other phosphinidene complex has ever been reported to add hydrogen. Actually, even free phosphines and related P-donor molecules fail to react with hydrogen under ordinary conditions. In this context we note that the first example of the oxidative addition of the relatively unreactive H−Si bond of silanes to a phosphinidene complex has been reported only very recently.[21] Further work is currently under progress to get a more precise picture of the remarkable hydrogenation of compound **3** and its potential relation with the steric demands of the PR* group.

In summary, we have shown that the steric pressure introduced by the 2,4,6-$C_6H_2{}^tBu_3$ group in the complexes [$Fe_2Cp_2(\mu$-PR$)(\mu$-CO$)(CO)_2$] having bent phosphinidene bridges has pronounced effects concerning its synthesis (stabilization of radical intermediates toward dehydrogenation), structure

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[15] Preparation of compound **5**: a dichloromethane solution (10 mL) of compound **3** (0.100 g, 0.188 mmol) was stirred in contact with air at room temperature for 1.5 h to give a brown solution yielding compound **5** (0.063 g, 61%) as a mixture of three isomers. Selected spectroscopic data for **5B**: ν(CO) (CH_2Cl_2) 1997 (vs), 1965 (w), 1774 (m) cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 312.0 ppm; ^{1}H NMR (CD_2Cl_2) δ 4.93 (s, 10H, Cp) ppm.

[16] Selected spectroscopic data for *trans*-**5T**: ν(CO) (CH_2Cl_2) 1964 (m), 1802 (w), 1769 (vs) cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2, 233 K) δ 432.5 ppm; ^{1}H NMR (CD_2Cl_2, 233 K) δ 5.01, 4.20 (2s, 2 × 5H, Cp) ppm.

[17] X-ray data for *trans*-**5T**: red crystals, monoclinic ($P2_1/c$), a = 10.8126(8) Å, b = 13.0255(11) Å, c = 20.5208(17) Å, β = 91.402(4)°, V = 2889.3(4) Å^3, T = 100 K, Z = 4, R = 0.0805 (observed data with $I > 2\sigma(I)$), GOF = 1.039.

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(geometrical distortions and changes in the coordination mode of ligands), thermal stability (intramolecular C−H bond activation), and general reactivity (hydrogenation, oxygenation). Further studies on the chemical behavior of compound **3** are now in progress to examine in detail the effects of steric pressure on the wide reactivity of this sort of phosphinidene complexes having bent phosphinidene bridges, with special emphasis on their intriguing ability for the activation of rather inert (H−H, H−C) single bonds.

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