may differ in detail from those in mononuclear platinum(II) complexes.[13]

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. **2a**, 100813-14-7; **2a**-^{13}C, 100813-19-2; **2b**, 74587-81-8; **3a**, 100813-15-8; **3a**-$^{13}C_2$, 100813-20-5; **3b**, 100813-16-9; **3b**-$^{13}C_2$, 100813-21-6; **4a**, 100813-17-0; **4a**-$^{13}C_3$, 100813-22-7; **4b**, 100813-18-1; **4b**-$^{13}C_3$, 100813-23-8.

Asymmetric Bonding Involving a Phosphinidene Complex. Synthesis and X-ray Crystal Structure of $[\{Fe(CO)_3P(4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2C_6H_2O)\}_2]$, an Organometallic Cyclobutadiene Analogue?

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Summary: The synthesis and structure of a new type of bridging phosphinidene–iron carbonyl complex, $[\{Fe(CO)_3P(4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2C_6H_2O)\}_2]$ (**1**), is reported. The structure of **1** shows that each phosphinidene ligand bridges two irons asymmetrically, with Fe–P distances of 2.202 (1) and 2.112 (1) Å, suggesting an isolobal comparison with cyclobutadiene.

A number of publications from this laboratory have described [1–4] the interesting products obtained from reactions of carbonylmetalate dianions with phosphorus chlorides containing bulky organic substituents. In all these cases the products involved either a diphosphene ligand bonded to a metal in one of several different ways as shown in **a**, **b**, or **c** or a phosphinidene ligand bridging two metals as shown in **d**. Phosphinidene complexes of type **d** and the side-on-bonded diphosphenes of type **e**, which were synthesized by other routes, had already been reported by a number of workers.[5] However, with the exception of the simultaneous disclosure of a complex of type **b** by the Cowley group,[5] the complexes **a**, **b**, and **c** were the first reported examples of their class. Huttner and co-workers have also reported further examples of type **a**[7a] and **b**[7b] complexes and also the structurally characterized type **f** complexes.[7a] More recently the cis isomer of complex **b** has been reported by both Huttner[7b] and Yoshifuji;[8] see also ref 4 for another example of a structurally characterized example of a cis diphosphene transition-metal cluster complex. For a general review of developments in the chemistry of heavier main-group multiple bonds see ref 9.

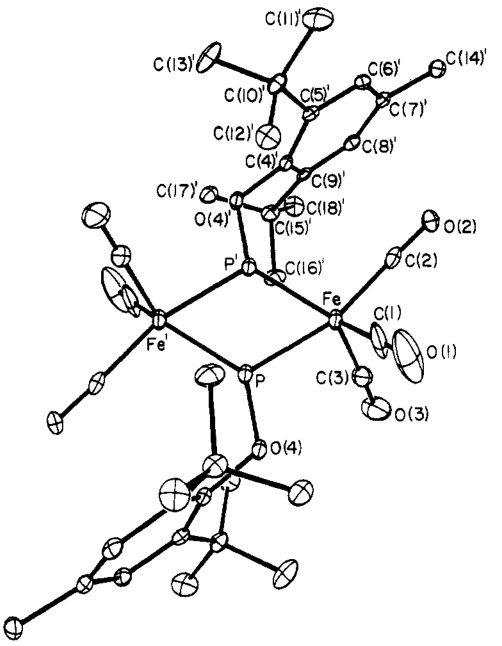
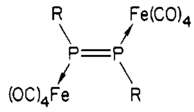
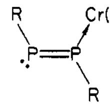


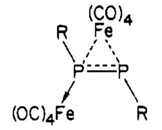
Figure 1. Computer-generated diagram of **1**. Important bond distances (Å) and angles (deg) not given in the text: Fe–C(1), –C(2), –C(3) = 1.793 (5), 1.812 (4), 1.821 (5); P–O(4) = 1.625 (3); C(1)–O(1) = 1.156 (7); C(2)–O(2) = 1.137 (5); C(3)–O(3) = 1.138 (5); P(4)–O(4) = 1.421 (5); FePFe′ = 113.5 (1); C(1)FeC(2) = 92.9 (2); C(1)FeC(3) = 106.0 (2); C(2)FeC(3) = 95.0 (2); PO(4)C(4) = 122.0 (2).



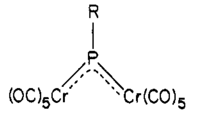
a



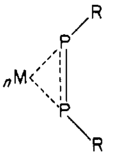
b



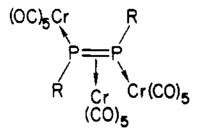
c



d



e



f

We now report the existence of a new type of structure obtained from the metal carbonylate/PCl_2R mixture which involves two asymmetrically bridging, roughly trigonal-planar phosphinidene groups linking two iron tricarbonyl fragments. This is the complex $[\{Fe(CO)_3P(4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2C_6H_2O)\}_2]$ (**1**). The structure of **1** was unexpected because the synthetic procedure was identical with that described for $[Fe(CO)_4\{\mu\text{-}Fe(CO)_4\}\{P(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)\}_2]$ (**2**) which has a side-on/end-on-bonded diphosphene ligand as depicted in **c**.[3] The only difference in the synthesis is a change at the 4-position of the phenoxy group from *tert*-butyl to methyl in this preparation.[10]

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† Fellow of the A. P. Sloan Foundation, 1985–1989.

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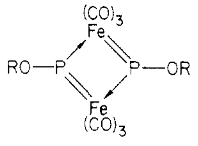
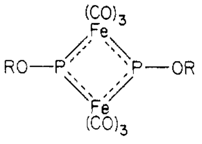
(10) The compounds $PCl_2(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)$ (**6**) and $PCl_2(2,4\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)$ (**7**) were readily synthesized by treatment of an ether solution of PCl_3 with slightly less than 1 equiv of the solid lithium aryloxide etherate (from *n*-BuLi and the phenol). Removal of LiCl and recrystallization from *n*-hexane gave the monosubstituted compounds **3** and **4** in ca. 50% yield. ^{31}P NMR for **3** and **4** showed singlets at +194 and +196 ppm. The melting points for **3** and **4** were 126 and 138 °C, respectively.

The experimental procedure involved dropwise treatment of an Et_2O (15 mL) suspension of $Na_2Fe(CO)_4 \cdot 1.5$dioxane (0.7 g, 2 mmol) with an Et_2O (15 mL) solution of $PCl_2(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)$ (0.64 g, 2 mmol) at 25 °C. Stirring for 12 h followed by removal of the volatiles in vacuo and extraction of the residue in *n*-hexane (25 mL) gave a red solution. Reduction of the volume in vacuo to 10 mL and cooling to −20 °C gave **1** as red-brown crystals: yield 0.07 g, 9%; mp 191–193 °C. The first indication of an unusual structure came from ^{31}P NMR. A single resonance at +564 ppm (relative to 85% H_3PO_4) was quite different from that of the AB pattern obtained for **2**. The complex can be handled in the air and shows no apparent decomposition after several days exposure. It is soluble in hydrocarbon solvents affording solutions that are also air-stable. Current mechanistic work in this group has shown, via ^{31}P NMR, that complexes of type **1** and **2** are present in the crude reaction mixtures of $Fe(CO)_4{}^{2-}$ and $RPCl_2$, R = $2,4,6\text{-}t\text{-}Bu_3C_6H_2O$ or $2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O$ in Et_2O. Moreover heating a solution of **2** in toluene to 70 °C results in a reduction in ^{31}P NMR AB pattern intensity and the appearance of a singlet at +563 ppm corresponding to a conversion of **2** into a type **1** complex.[11]

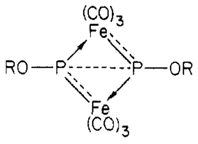
The structure of the complex was solved by single-crystal X-ray diffraction[12] and is shown in Figure 1. It consists of isolated neutral molecules with no short intermolecular contacts. Each iron atom may be regarded as having severely distorted (e.g., PFeP′ = 66.5 (1)°) trigonal-bipyramidal coordination to three carbonyl ligands and to two phosphorus atoms. The main feature of interest in the molecule involves the bonding between iron and the phosphinidene ligand. There are two Fe–P distances, Fe–P = 2.202 (1) Å and Fe–P′ = 2.112 (1) Å. The former is slightly shorter than bond lengths found in other $Fe(CO)_4$ phosphine or diphosphene complexes. For example, a terminal Fe–P distance of 2.226 (1) Å is found in **a** where R = $CH(SiMe_3)_2$ and in **c** where R = $2,4,6\text{-}t\text{-}Bu_3C_6H_2O$.[1,3] The latter has considerably longer Fe–P bridging distances of 2.362 (2) and 2.347 (2) Å. The shorter Fe–P′ bond length is very similar to those found in some phosphenium complexes where there is thought to be an Fe–P multiple bond.[13] The difference in the Fe–P and –P′ bond lengths and the close to planar geometry at phosphorus suggests that the bonding may be represented schematically by **g** rather than the expected symmetrically bound phosphinidene complex in **h**. It could be argued that the difference in Fe–P and –P′ distances is due to differences in axial and equatorial bonding. We think this unlikely since there is no example of such a large difference between Fe–L(axial) and Fe–L(equatorial) bonds.[14] There is no interaction between the Fe atoms, the distance being greater than 3.6 Å. The P–P′ separation, 2.367 (2) Å, on the other hand, is short enough to be considered a long P–P single bond (usual P–P single bond distances are ca. 2.2–2.4 Å).[15] This would imply that the schematic representation given by **i** may be closer to the actual bond order present. However it is not possible to decide whether the close P···P contact is imposed by the complex geometry or an inherent P–P bond. The core of the molecule defined by P(1), P(1)′, O(1), O(1)′, Fe, and Fe′ is very close to planar.[16]



g



h



i

Another view of the bonding in **1** arises from the isolobal relationship[17] between $Fe(CO)_3$ and CH^+ or PR and CH^-. A complex of composition $[\{(OC)_3FePR\}_n]$ should show a resemblance to $[(CH)_{2n}]$. This relationship has already been demonstrated by Vahrenkamp and co-workers in a number of related complexes. These are the tetrahedrane analogue $[\{(OC)_3FeP\text{-}t\text{-}Bu\}_2]$[18] (**3**), the cubane analogue $[\{(OC)_3FeAsMe\}_4]$[19] (**4**), and the octabisvalene analogue $[\{(OC)_3FePMe\}_4]$[20] (**5**). The geometry seen in **1**, which suggests an analogy to cyclobutadiene (c-$(CH)_4$), is in sharp contrast to the tetrahedrane (also $(CH)_4$) configuration suggested by **3**. It may be that the bulky aryloxide ligand in **1** disfavors the cis coordination of a diphosphene seen in **3** and causes weakening of the P–P bond, thereby promoting the open structure seen in **1**.[21]

The complex is also diamagnetic, and this is supported by the ^1H and ^{31}P NMR data. In addition a hexane solution of **1** was ESR inactive at room temperature. The larger downfield shift of the ^{31}P NMR of phosphinidene relative to diphosphene[1,3] complexes also agrees with the bonding shown in **g**.[22]

The IR (Nujol mull) shows a complex pattern 2052 (sh), 2041 (sh), 2021 (s), 2007 (s), 1991 (s), and 1961 (s) cm^{-1}. The ^1H NMR ($CDCl_3$, Me_4Si internal standard) gives a singlet at 1.6 ppm (18 H), a singlet at 2.2 ppm (3 H), and

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(11) Flynn, K. M.; Power, P. P., unpublished observations.

(12) A red-brown crystal of 1, having the dimensions 0.15 × 0.50 × 0.60 mm, was mounted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. With Mo Kα radiation (λ = 0.71069 Å) and the crystal cooled to 140 K, crystal data were as follows: monoclinic, space group $P2_1/n$; a = 15.840 (2) Å, b = 8.569 (1) Å, c = 15.996 (2) Å; β = 119.60 (1)°; Z = 2; μ = 8.97 cm^{-1} (range of absorption correction factors 1.21–1.80). Data were collected to $2\theta_{max}$ of 50° with an ω scan technique. A total of 3271 unique data were collected of which 2490 had $I > 3\sigma(I)$. Scattering factors and corrections for anomalous scattering were from Vol. IV of the "International Tables". Computer programs were those of SHELXTL, Version 3, July 1981 package. The structure was solved by Patterson methods. The R value with anisotropic thermal parameters (with H) = 4.34% and R_w = 4.65%. There is some rotational disorder in the *tert*-butyl groups which is reflected in the larger thermal ellipsoids of these groups. Tables of atomic coordinates, thermal parameters, and bond lengths and angles are available as supplementary material.

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(16) Deviations (Å) from this plane: P, −0.022; P′, +0.022; Fe, −0.002; Fe′, +0.002; O(4), +0.009; O(4)′, −0.009.

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(21) Another example of asymmetry in phosphinidene complexes arose after this work had been submitted. We were informed by Professor A. Cowley of the synthesis of the phosphinidene complex $[2,4,5\text{-}t\text{-}Bu_3C_6H_2P\{(Co(CO)(\eta^5\text{-}C_5H_5)_2\}]$. This interesting compound has an open structure but displays asymmetry in the angles but not in the bond lengths around phosphorus. We thank Professor Cowley for making data on this compound available prior to publication.

(22) For example, $[Cr(CO)_2]_2P\text{-}t\text{-}Bu$, ^{31}P NMR 1362 ppm: Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.* **1984**, *263*, C33. $Ph_2P_2\text{-}[Cr(CO)_5]_2$, ^{31}P NMR 927 ppm: ref 7a and Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem. Suppl.* **1983**, 1477. This value was later amended to 369 ppm, see ref 7b.

a singlet at 7.09 ppm (2 H).

Acknowledgment. This work was supported by a grant from the National Science Foundation CHE-8116355. K.M.F. gratefully acknowledges the University of California, Davis for an E. C. Anthony Fellowship.

Registry No. **1**, 100681-67-2; **2**, 87830-08-8; **6**, 796-62-3; **7**, 789-54-8; 2,4,6-*t*-$Bu_3C_6H_2OH$, 732-26-3; 2,4-*t*-Bu_2-4-MeC_6H_2OH, 128-37-0; PCl_3, 7719-12-2; $Na_2Fe(CO)_4$, 14878-31-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, H coordinates and thermal parameters, and observed and calculated structure factor tables for compound **1** (19 pages). Ordering information is given on any current masthead page.

The Determination of the Mn–Mn Bond Strength in $Mn_2(CO)_{10}$ Using Pulsed Time-Resolved Photoacoustic Calorimetry

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Summary: The enthalpy of reaction for the photodissociation of $Mn_2(CO)_{10}$ in several solvents has been measured by pulsed time-resolved photoacoustic calorimetry. Using known quantum yield measurements for Mn–Mn homolysis and Mn–CO ligand dissociation, the Mn–Mn bond strength is determined to be 38.0 ± 5 kcal/mol.

Crucial to the development of metal cluster chemistry is a knowledge of the metal–metal and metal–ligand bond strengths in at least a few transition-metal cluster complexes. The difficulties in obtaining such information are illustrated with the example of the metal–metal bond strength in $Mn_2(CO)_{10}$, the first unsupported metal bond to be characterized.[1] The dissociation energy for the metal–metal bond has been obtained from thermochemical measurements (16 kcal/mol,[2] 22.5 kcal/mol,[3] and 34 ± 13 kcal/mol[4]), electron-impact mass spectroscopic data[5-9] (values ranging from 19 to 28 kcal/mol), kinetic measurements in solution[10-12] (36.8 kcal/mol), and recently a combination of ICR and photoelectron spectroscopy[13] (41 ± 9 kcal/mol^{-}). This disturbing scatter of values points to the difficulty of obtaining specific bond energies in transition-metal complexes.

The metal–ligand bond dissociation energy in $Mn(CO)_5L$ complexes has been investigated,[3,14] but the absolute Mn–L bond energies are based on the value estimated from D(Mn–Mn) in $Mn_2(CO)_{10}$ and are, therefore, themselves only as reliable as this estimate.

Scheme I

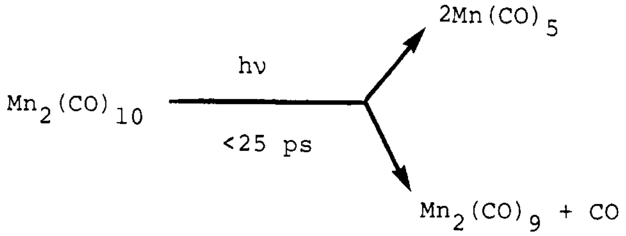

Table I. Enthalpies of Reaction in Various Solvents[a]

solv	ΔH_r,[b] kcal/mol
hexane (C_6H_{14})	14.0
cyclohexane (C_6H_{12})	13.6
THF	11.9
acetonitrile (CH_3CN)	11.5

[a] Photolysis of $Mn_2(CO)_{10}$ solutions (OD < 0.4) at room temperature with 337-nm excitation. [b] Errors are ±1.0 kcal/mol.

In this communication, we report an estimate of the D(Mn–Mn) in $Mn_2(CO)_{10}$ in solution obtained by using pulsed time-resolved photoacoustic calorimetry. This is a method whereby reaction enthalpies for ground-state reactants forming stable or transient photoproducts are measured. In this experiment, a fraction of the energy absorbed by the sample from an incident light beam is ultimately released as heat. Local thermal expansion generates pressure waves which can be detected by a transducer. An in-depth analysis of the theory and experiment has been reported.[15]

Quantitative interpretation of the heat deposition measured in this experiment requires a knowledge of the mechanism and kinetics of the photochemical reaction under study. Fortunately, the photochemistry of $Mn_2(CO)_{10}$ is one of the best studied among transition-metal cluster carbonyls.[16] Kinetic experiments in several laboratories[17-19] are consistent with the mechanism outlined in Scheme I. Picosecond flash photolysis experiments performed in our laboratory[17] showed that photolysis of $Mn_2(CO)_{10}$ leads to the formation of $Mn(CO)_5$ and $Mn_2(CO)_9$ within 25 ps of excitation. Quantum yield measurements for the dissociation of $Mn_2(CO)_{10}$ are available, yet the literature values are varied.

In the study reported herein, the enthalpy of reactions ΔH_r of the above photoprocess were measured[20,21] in a variety of solvents at room temperature and are listed in Table I. Simply, ΔH_r is determined by comparison of the integrated photoacoustic waveform obtained from photolysis of $Mn_2(CO)_{10}$ to that obtained from photolysis of a standard, i.e., ferrocene, with known photophysical and

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(19) Meyer, T. J. *Chem. Rev.*, in press, and references therein.

(20) Freshly sublimed $Mn_2(CO)_{10}$ was dissolved in deoxygenated spectrograde solvents. Samples were degassed with argon for 10 min and then maintained under an argon atmosphere during the experiment. Photolysis was initiated by a nitrogen laser (5 ns, 337 nm, ≤20 μJ, 2-mm diameter). Sample absorbances did not change during photolysis, suggesting that no decomposition occurred at these low fluence levels.

(21) On the time scale of the laser experiment (≃1 μs), both recombination processes, $2Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ and $Mn_2(CO)_9 + CO \rightarrow Mn(CO)_{10}$, are slow and consequently do not contribute to the overall enthalpy of reaction.[18,25]

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