

of the  $C_6F_4Br$  ring into the second axial site.

For comparison the bond lengths within the core are given in Table IV together with those of previously published ortho-metalated dimers. Clearly the Rh-Rh bond length is well within the range spanned by differences in axial substituents.

An especially noteworthy feature of this molecule is the unprecedented way in which double-axial ligation is achieved. On one end of the dimer we find an acetate group in a chelating mode so that in addition to filling one equatorial position it also fills the adjacent axial position. Although it is not a common one, there are precedents for this arrangement.<sup>7,8</sup> The axial site on the other metal atom is occupied by a Br atom attached to one of the phosphine phenyl rings. This Br atom, despite its being an integral part of the perfluorophenyl ring, has a contact distance with the Rh which is, by all standards, a strong axial ligation.

**Chemical Reaction.** The reaction of dirhodium tetraacetate with  $P(C_6H_5)_2(C_6F_4Br)$  is fundamentally similar to its reaction with triphenylphosphine, but there are a number of differences in detail. Two phosphine ligands are added to the dirhodium unit, but only one becomes ortho metalated, and in neither one is the bromine-carbon bond broken.

One  $P(C_6H_5)_2(C_6F_4Br)$  molecule becomes ortho metalated on one of its phenyl rings by formal proton transfer to an acetate anion, which is entirely eliminated from the product. As we noted earlier,<sup>4</sup> this formal acid-base reaction is not favorable and the overall transformation must be thermodynamically driven by other factors, such as the (presumably favorable) replacement of the two Rh-O bonds to a bridging acetate group by the Rh-P and Rh-C bonds in the product.

In the present case, the first ortho metalation is not followed by a second one. Instead, the second molecule of  $P(C_6H_5)_2(C_6F_4Br)$  only partially displaces an acetate group whereby an equatorial Rh-P bond is formed. However, this phosphine molecule then orients itself so that its bromine atom can form a rather good donor bond to the same rhodium atom at the axial position. The partially displaced acetate ion then occupies the neighboring equatorial position and also fills the other axial site.

A question that naturally arises is: Why has not the second molecule of phosphine undergone ortho metalation in this case, as in the earlier one?<sup>4</sup> We suggest, as a tentative answer, that molecule **2** does not react further in refluxing toluene because it is stabilized by the internal formation of axial bonds which would be partly or entirely sacrificed if the second phosphine became ortho metalated in the same way as the first one. In pure toluene there are no exogenous axial ligands and thus compound **2** is stable. In the reaction of  $Rh_2(O_2CCH_3)_4$  with  $PPh_3$  in refluxing acetic acid, the acetic acid molecules were able to occupy the axial positions. We are currently doing further work to see how important this medium effect is and specifically to see if we can find a way to drive compound **2** to undergo the second ortho metalation and thus produce a product of the type  $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_4Br)]_2 \cdot L_2$  where L is some suitable axial ligand. Work done so far shows that both **1** and **2** can undergo a variety of reactions and that conditions will have to be carefully controlled to achieve a specific predetermined result.

**Acknowledgment.** We thank the National Science Foundation and C.A.I.C.Y.T for support.

**Registry No.** **1**, 100702-00-9; **2**, 100702-01-0;  $Rh_2(O_2CCH_3)_4 \cdot 2MeOH$ , 41772-64-9; Rh, 7440-16-6.

**Supplementary Material Available:** Complete tables of bond distances and angles, anisotropic displacement parameters, and structure factors (16 pages). Ordering information is given on any current masthead page.

(7) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935.  
(8) Chisholm, M. H.; Extnie, M. W.; Cotton, F. A.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4683.

## Communications

### The Easy Interconversion of Diplatinum(I) and Platinum(0)-Platinum(II) Complexes by Reversible Carbonyl Addition

Alistair J. McLennan and Richard J. Puddephatt\*

Department of Chemistry, University of Western Ontario  
London, Canada N6A 5B7

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**Summary:** The complexes  $[HPt(\mu-PP)_2PtCO]^+$ , PP =  $Et_2PCH_2PEt_2$  or  $Ph_2PCH_2PPh_2$ , add reversibly and very rapidly at room temperature one or two carbonyl groups to give  $[HPT(\mu-PP)_2Pt(CO)_2]^+$  and  $[H(CO)Pt(\mu-PP)_2Pt(CO)_2]^+$ . Evidence is presented that the reactions essentially involve disproportionation of diplatinum(I) to give the first reported platinum(0)-platinum(II) species and the results give new insights into the mechanism of ligand substitution at platinum(I).

Mixed-valence compounds of platinum are of consid-

erable importance, but there are very few mixed-valence molecular compounds and no platinum(0)-platinum(II) derivatives.<sup>1-3</sup> This article describes how very easy disproportionation of diplatinum(I) complexes to give platinum(0)-platinum(II) complexes can be induced by addition of carbon monoxide, as shown in Scheme I.

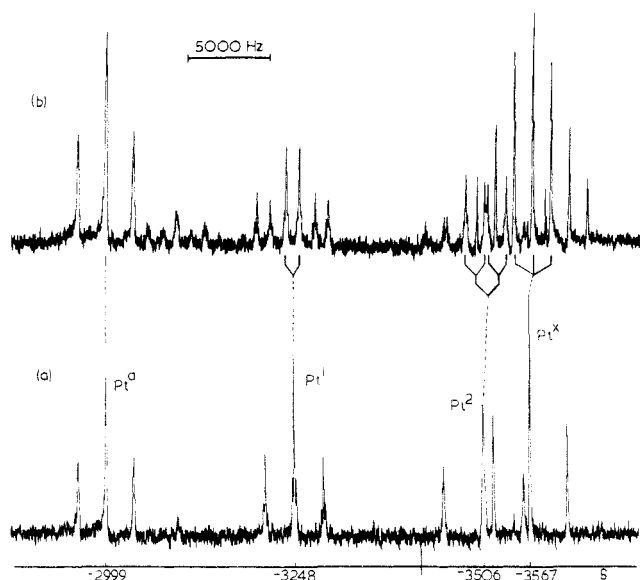
The reversible addition of CO to complexes **2**, prepared as shown in Scheme I,<sup>4</sup> is rapid on the NMR time scale at room temperature, and so the new complexes **3** and **4** could not be isolated but were identified by multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>195</sup>Pt) NMR in acetone-*d*<sub>6</sub> at -90 °C.<sup>4,5</sup>

(1) Clark, R. J. H. *Chem. Soc. Rev.* **1985**, 219.

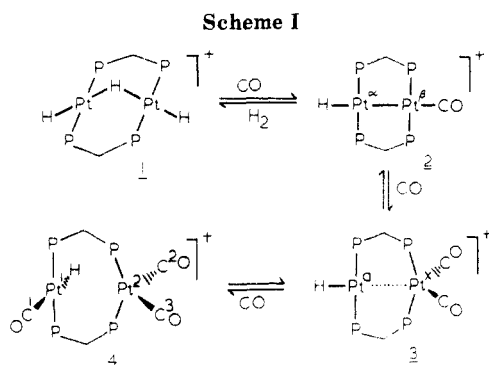
(2) Balch, A. L. *Comments Inorg. Chem.* **1984**, *3*, 51.

(3) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793.

(4) Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W. *Organometallics* **1982**, *1*, 1421. Manojlović-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1981**, *219*, 129.



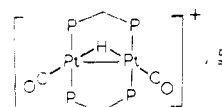
**Figure 1.**  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra ( $-90^\circ\text{C}$ , 64.3 MHz) of reaction mixtures containing largely **3a** and **4a**: (a) prepared from  $^{12}\text{CO}$  and (b) prepared from  $^{13}\text{CO}$ . The multiplicities from  $^1\text{J}(\text{Pt}^{13}\text{C})$  coupling, which are indicated below spectrum b, show that  $\text{Pt}^0$ ,  $\text{Pt}^1$ ,  $\text{Pt}^2$ , and  $\text{Pt}^x$  are bound to 0, 1, 2 (nonequivalent), and 2 (equivalent) CO ligands, respectively.



Signals in the  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{195}\text{Pt}$  NMR spectra were assigned to **2**, **3**, or **4** (Scheme I) by monitoring changes in relative intensities with CO pressure, and the structures of the new compounds **3** and **4** were deduced from the  $^{13}\text{C}$  and  $^{195}\text{Pt}$  NMR spectra of the  $^{13}\text{CO}$ -substituted derivatives **3\*** and **4\*** (asterisk indicates  $^{13}\text{CO}$  labeled species). For example, Figure 1 shows the  $^{195}\text{Pt}$  NMR spectra of an equilibrium mixture containing largely **3a** and **4a** prepared from either  $^{12}\text{CO}$  or  $^{13}\text{CO}$ . The multiplicities of the  $^{195}\text{Pt}$  NMR signals due to the extra coupling  $^1\text{J}(\text{PtC})$  for **3a\*** and **4a\*** define the number of carbonyl groups bound to each platinum center. There was no evidence for long-range

$^{195}\text{Pt}\text{--}^{13}\text{C}$  coupling in either **3a\*** or **4a\***, which we take to be evidence against the presence of a bridging or semi-bridging carbonyl, such as is seen in  $[\text{Rh}_2(\text{CO})_3(\mu\text{-dppm})_2]$ ,<sup>6,7</sup> which is isoelectronic with **3**, or, for the isonitrile case, in  $[\text{Ni}_2(\text{MeNC})_4(\mu\text{-dppm})_2]^{2+}$ , which is isoelectronic with **4**.<sup>8</sup> Cleavage of the Pt–Pt bond of **2** on formation of **3** or **4** is indicated by major changes in NMR parameters.<sup>9,10</sup> For example,  $^1\text{J}(\text{PtPt})$  in **2a** is 2400 Hz, but this coupling is not resolved and is certainly less than 200 Hz in **3a**, and is only 350 Hz in **4a**.<sup>10</sup> The Pt–Pt bond of **2a** exerts a significant trans influence and  $^1\text{J}(\text{PtH}) = 1054$ , but in **3a**  $^1\text{J}(\text{PtH}) = 1380$  Hz and this indicates that a ligand with a very weak trans influence is trans to hydride.<sup>9,10</sup> We suggest that a weak donor–acceptor bond between the Pt(0) center  $\text{Pt}^x$  and Pt(II) center  $\text{Pt}^a$  is present in **3**.

The pure complexes **2** were not fluxional at room temperature, but fluxionality could be induced by the presence of trace amounts of CO. For example, the PtH signal of **2a** appeared as a 1:8:18:8:1 quintet [ $\delta -6.37$  ( $^1\text{J}(\text{PtH}) = 510$ )] in the presence of small amounts of CO, and a single  $^{31}\text{P}$  resonance was observed; on cooling to  $-90^\circ\text{C}$  the spectrum of pure **2a** was frozen out.<sup>5</sup> This experiment shows that a symmetrical species with a  $\text{Pt}_2(\mu\text{-H})$  groups, presumably **5**, is kinetically accessible at room temperature.<sup>11</sup>



There are a number of novel aspects of this work: 1. It shows how easy disproportionation of a diplatinum(I) complex, **2**, to give the first reported platinum(0)–platinum(II) complexes **3** or **4** can be induced by ligand addition. 2. This behavior is different from that displayed<sup>12</sup> by the symmetrical diplatinum(I) complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$ , which can add CO to give either  $[\text{Pt}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-dppm})_2]$  or  $[\text{Pt}_2\text{Cl}(\text{CO})(\mu\text{-dppm})_2]^+\text{Cl}^-$ , both of which maintain equal oxidation states for the two platinum centers. 3. The reversible reaction  $2 + \text{CO} \rightleftharpoons 3$  shows clearly the mechanism of CO for CO ligand substitution in complex **2**, and such ligand substitution is much faster than in other diplatinum(I) complexes.<sup>13</sup> It seems that the easy cleavage of the Pt–Pt bond of **2** as CO addition occurs stabilizes the intermediate **3** in ligand substitution and illustrates how mechanisms of ligand substitutions

(6) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* 1985, 24, 1285.

(7) Sutherland, B. R.; Cowie, M. *Organometallics* 1985, 4, 1637. These authors report the complex  $[\text{Ir}_2(\text{CO})_3(\mu\text{-dppm})_2]$  which gives three separate carbonyl resonances in the  $^{13}\text{C}$  NMR at low temperature whereas for **3** only one carbonyl resonance was observed. This is expected if  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$  has a semibridging carbonyl whereas **3** does not. Semibridging carbonyls are characterized by CO stretching frequencies at ca.  $1850\text{ cm}^{-1}$ ,<sup>8</sup> but we have not seen a band in this region for **3**.

(8) DeLaet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* 1985, 4, 954.

(9) For example,  $^1\text{J}(\text{PtH})$  values for *trans*- $[\text{PtHL}(\text{PEt}_3)_2]^+$  are 1450 (L = acetone), 1369 (L = I<sup>-</sup>), 1322 (L = NO<sub>3</sub><sup>-</sup>), 1003 (L = NO<sub>2</sub><sup>-</sup>), and 967 (L = CO). Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* 1974, 13, 2213. Church, M. J.; Mays, M. J. *J. Chem. Soc. A* 1968, 3074. Powell, J.; Shaw, B. L. *J. Chem. Soc.* 1965, 3879.

(10) It should be noted, however, that there is no clear correlation of  $^1\text{J}(\text{PtPt})$  with PtPt bond distance. Pregosin, P. S. *Coord. Chem. Rev.* 1982, 44, 247.

(11) Complex **5** could be formed in undetectably low concentration by intramolecular rearrangement of **3** or by attack of CO at the hydrido-platinum end ( $\text{Pt}^x$ ) of **2**. No  $^1\text{J}(\text{PtC})$  coupling could be resolved at room temperature, and only a broad  $^{13}\text{C}$  resonance was observed. Note that the interconversions of **2**, **3**, and **4** do not lead to hydride exchange between platinum centers.

(12) Puddephatt, R. J. *J. Chem. Soc. Rev.* 1983, 99.

(13) Shimura, M.; Espenson, J. H. *Inorg. Chem.* 1984, 23, 4069.

(5) Key NMR data in acetone-*d*<sub>6</sub> at  $-90^\circ\text{C}$  (references Me<sub>4</sub>Si, (MeO)<sub>3</sub>PO, and K<sub>2</sub>PtCl<sub>4</sub>). **2a\***:  $\delta -6.06$  [dt,  $^1\text{J}(\text{PtH}) = 1054$ ,  $^2\text{J}(\text{PH}) = 12$ ,  $^3\text{J}(\text{HCO}) = 16$  Hz, PtH];  $+191.0$  [s,  $^1\text{J}(\text{PtC}) = 1105$ ,  $^2\text{J}(\text{PtC}) = 177$  Hz, PtCO];  $+3.51$  [t,  $^1\text{J}(\text{PtP}) = 2464$  Hz, P<sup>a</sup>];  $-1.00$  [t,  $^1\text{J}(\text{PtP}) = 2968$  Hz, P<sup>b</sup>];  $-3095$  [dt,  $^2\text{J}(\text{PtP}) = 95$ ,  $^1\text{J}(\text{PtPt}) = 2400$  Hz, Pt<sup>a</sup>];  $-2667$  [dt, Pt<sup>b</sup>]. **3a\***:  $-5.34$  [m,  $^1\text{J}(\text{PtH}) = 1380$  Hz, PtH];  $+178.10$  [s,  $^1\text{J}(\text{PtC}) = 1570$  Hz, PtCO];  $+18.30$  [t,  $^1\text{J}(\text{PtP}) = 2390$ , P<sup>a</sup>];  $-22.01$  [t,  $^1\text{J}(\text{PtP}) = 3180$  Hz, P<sup>b</sup>];  $-2999$  [t, Pt<sup>a</sup>];  $-3567$  [tt, Pt<sup>b</sup>]. **3b\***:  $-6.19$  [s,  $^1\text{J}(\text{PtH}) = 1326$  Hz, PtH];  $+178.15$  [s,  $^1\text{J}(\text{PtC}) = 1340$  Hz, PtCO];  $+14.30$  [t,  $^1\text{J}(\text{PtP}) = 2700$  Hz, P<sup>a</sup>];  $-17.05$  [t,  $^1\text{J}(\text{PtP}) = 3240$  Hz, P<sup>b</sup>];  $-3093$  [br, Pt<sup>a</sup>];  $-3391$  [br, Pt<sup>b</sup>]. **4a\***:  $-7.14$  [d,  $^1\text{J}(\text{PtH}) = 840$ ,  $^2\text{J}(\text{CH}) = 59$  Hz, PtH];  $+181.66$  [s,  $^1\text{J}(\text{PtC}) = 1100$  Hz, C<sup>1</sup>O];  $+172.67$  [s,  $^1\text{J}(\text{PtC}) = 1560$  Hz, C<sup>2</sup> or C<sup>3</sup>O];  $+180.84$  [s,  $^1\text{J}(\text{PtC}) = 1860$  Hz, C<sup>2</sup> or C<sup>3</sup>O];  $+1.49$  [m,  $^1\text{J}(\text{PtP}) = 2460$  Hz, P<sup>1</sup>];  $-20.72$  [m,  $^1\text{J}(\text{PtP}) = 3490$  Hz, P<sup>2</sup>];  $-3248$  [dt,  $^1\text{J}(\text{PtPt}) = 350$  Hz, Pt<sup>1</sup>];  $-3506$  [ddt, Pt<sup>2</sup>]. **4b\***:  $-8.40$  [d,  $^1\text{J}(\text{PtH}) = 652$ ,  $^2\text{J}(\text{CH}) = 58$  Hz, PtH];  $+183.92$  [s,  $^1\text{J}(\text{PtC}) = 1135$  Hz, C<sup>1</sup>O];  $+172.88$  [s,  $^1\text{J}(\text{PtC}) = 1575$  Hz, C<sup>2</sup> or C<sup>3</sup>O];  $+183.40$  [s,  $^1\text{J}(\text{PtC}) = 1835$  Hz, C<sup>2</sup> or C<sup>3</sup>O];  $+7.89$  [m,  $^1\text{J}(\text{PtP}) = 2840$  Hz, P<sup>1</sup>];  $-9.12$  [m,  $^1\text{J}(\text{PtP}) = 3560$  Hz, P<sup>2</sup>];  $-3228$  [dt,  $^1\text{J}(\text{PtPt}) = 530$ , Pt<sup>1</sup>];  $-3386$  [ddt, Pt<sup>2</sup>].

may differ in detail from those in mononuclear platinum-(II) complexes.<sup>13</sup>

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

**Registry No.** 2a, 100813-14-7; 2a-<sup>13</sup>C, 100813-19-2; 2b, 74587-81-8; 3a, 100813-15-8; 3a-<sup>13</sup>C<sub>2</sub>, 100813-20-5; 3b, 100813-16-9; 3b-<sup>13</sup>C<sub>2</sub>, 100813-21-6; 4a, 100813-17-0; 4a-<sup>13</sup>C<sub>3</sub>, 100813-22-7; 4b, 100813-18-1; 4b-<sup>13</sup>C<sub>3</sub>, 100813-23-8.

### Asymmetric Bonding Involving a Phosphinidene Complex. Synthesis and X-ray Crystal Structure of $[[\text{Fe}(\text{CO})_3\text{P}(4\text{-Me-2,6-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{O})_2]_2]$ , an Organometallic Cyclobutadiene Analogue?

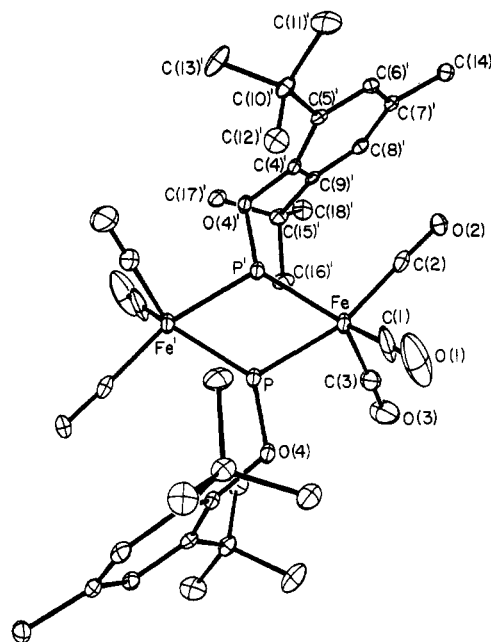
Kathy M. Flynn, Ruth A. Bartlett, Marilyn M. Olmstead, and Phillip P. Power\*<sup>†</sup>

Department of Chemistry, University of California Davis, California 95616

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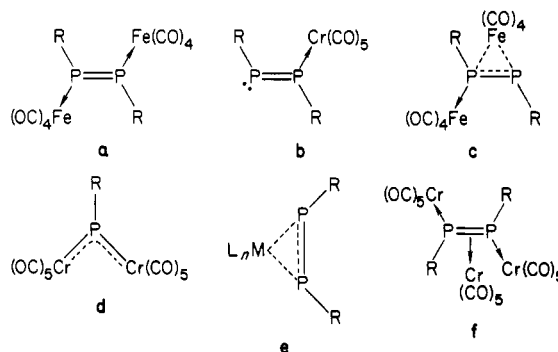
**Summary:** The synthesis and structure of a new type of bridging phosphinidene-iron carbonyl complex,  $[[\text{Fe}(\text{CO})_3\text{P}(4\text{-Me-2,6-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{O})_2]_2]$  (1), is reported. The structure of 1 shows that each phosphinidene ligand bridges two irons asymmetrically, 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<sup>1-4</sup> 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.<sup>5</sup> However, with the exception of the simultaneous disclosure of a complex of type b by the Cowley group,<sup>5</sup> 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<sup>7a</sup> and b<sup>7b</sup> complexes and also the structurally characterized type f complexes.<sup>7a</sup> More recently the cis isomer of complex b has been reported by both Huttner<sup>7b</sup> and Yoshifuji;<sup>8</sup> see also ref 4 for another example of a struc-



**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); Fe-PFe' = 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).

turally 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.



We now report the existence of a new type of structure obtained from the metal carbonylate/ $\text{PCl}_2\text{R}$  mixture which involves two asymmetrically bridging, roughly trigonal-planar phosphinidene groups linking two iron tricarbonyl fragments. This is the complex  $[[\text{Fe}(\text{CO})_3\text{P}(4\text{-Me-2,6-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{O})_2]_2]$  (1). The structure of 1 was unexpected because the synthetic procedure was identical with that described for  $[[\text{Fe}(\text{CO})_4]_2\mu\text{-Fe}(\text{CO})_4]\{\text{P}(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})_2\}_2]$  (2) which has a side-on/end-on-bonded diphosphene ligand as depicted in c.<sup>3</sup> 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.<sup>10</sup>

<sup>†</sup> Fellow of the A. P. Sloan Foundation, 1985-1989.

(1) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1983, 105, 2085.

(2) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1983, 105, 7460.

(3) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1983, 105, 7750.

(4) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1984, 106, 1495.

(5) Huttner, G.; Müller, H.-D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 705. Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.* 1984, 263, C33. Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* 1976, 122, 281. Cannillo E.; Coda, A.; Prout, K.; Daran, J. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1977, B33, 2608. Deppisch, B.; Schäfer, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* B38, 748. Dixon, K. R. *J. Chem. Soc., Chem. Commun.* 1982, 932. Green, J. C.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* 1974, 212.

(6) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* 1983, 105, 7751.

(7) (a) Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 977. (b) Lang, H.; Orama, O.; Huttner, G. *J. Organomet. Chem.* 1985, 291, 293.

(8) Yoshifuji, M.; Hashida, T.; Inamoto, N.; Hirotsu, K.; Horiuchi, T.; Higuchi, T.; Ito, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 211.

(9) Cowley, A. H. *Polyhedron* 1984, 3, 389.

(10) The compounds  $\text{PCl}_2(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})$  (6) and  $\text{PCl}_2(2,4,6\text{-}t\text{-Bu}_2\text{-4-MeC}_6\text{H}_2\text{O})$  (7) were readily synthesized by treatment of an ether solution of  $\text{PCl}_3$  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. <sup>31</sup>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.