

in the triplet systems can be explained in terms of the electronic structure of the intermediate complex.

**Concluding Remarks.** We have described the ionic photodissociation processes of electron donor-acceptor systems as studied by nanosecond laser photolysis. Dissociative states, solvent effects on dissociation yield, and relationships between the yield and the redox potential of component molecules have been examined, and a simplified but satisfactory model of dissociation mechanism is presented. In this model, electron transfer of fluorescer-quencher systems, or electronic and vibrational relaxations from the excited Franck-Condon state of charge-transfer complexes, leads to formation of a transient ionic complex, where dissociation to ions and other radiationless transitions compete with each other. The nature of the transient ionic complex and the character of the latter transitions are discussed in detail. The proposed model should be examined further by using the absorption spectra of the

complex in question, which will be possible in the near future by using picosecond laser photolysis method. Additional useful information is being obtained from magnetic field effects on the relevant processes.<sup>42</sup> For establishing a general concept of ionic photodissociation, various kinds of donor-acceptor systems should be examined by these experiments, since this process is very sensitive to the chemical properties of the component molecules.

*We thank our co-workers, whose names appear in the references, for their efforts. Thanks are also due the Japanese Ministry of Education, Culture and Science for their financial support. The kind advice of the editors and reviewers concerning English usage is gratefully acknowledged.*

(42) K. Schulten, H. Staerk, A. Weller, H.-J. Werner, and B. Nickel, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 371 (1976); H.-J. Werner, H. Staerk, and A. Weller, *J. Chem. Phys.*, **68**, 2419 (1978); U. Steiner, *Z. Naturforsch. A*, **34a**, 1093 (1979); U. Steiner, *Chem. Phys. Lett.*, **74**, 108 (1980).

## "Ligand-Free" Platinum Compounds

F. GORDON A. STONE

*Department of Inorganic Chemistry, The University, Bristol BS8 1TS, United Kingdom*

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Transition metals readily form complexes with ligated carbon atoms, and platinum is no exception. Indeed, organo derivatives of this metal<sup>1</sup> were studied intermittently for over a century prior to the discovery of ferrocene. Recognition of the sandwich structures of the metallocenes led to burgeoning research on  $\pi$  complexes and carbonyl compounds. In parallel with these developments it was discovered<sup>2</sup> that many organo-platinum species could be prepared from platinum halide complexes and organolithium or Grignard reagents. Although this route has afforded numerous alkyl-, aryl-, alkenyl-, or allylplatinum species, it is limited in scope. Indeed, the ease with which stable organo-platinum compounds are isolated from metathetical reactions between platinum halides and carbanion reagents has perhaps inhibited progress by causing investigators to focus on this method of carbon-platinum bond synthesis to the detriment of other possibilities. Certainly the development of organoplatinum chemistry has been less broadly based than that of the other subgroup 8 metals, notably nickel. There have been two reasons for this state of affairs.

Nickel forms a mononuclear tetracarbonyl, reasonably stable at room temperature but with CO ligands replaceable by other organic groups, e.g. RNC, RC $\equiv$ CR,  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>, or  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>.<sup>3</sup> In contrast [Pt(CO)<sub>4</sub>] is a laboratory curiosity, existing only in rare-gas matrices at very low temperatures,<sup>4</sup> and so is unsuitable for use as a reagent in synthesis. Even [Ni(CO)<sub>4</sub>] has its limita-

tions for use in preparing other organonickel compounds because of its toxicity and the difficulty of replacing all four CO groups in certain reactions where this would be a desirable end result. Hence reports commencing in 1960 that nickel formed compounds in which olefinic groups are the only ligands and, moreover, that these ligands were very labile proved to be of seminal importance.<sup>5</sup> Consequently, complexes such as [Ni(cod)<sub>2</sub>] (cod = 1,5-cyclooctadiene), and [Ni(cdt)] (cdt = *trans*-1,*trans*-5,*trans*-9-cyclododecatriene) have become standard reagents.<sup>3</sup> Their high reactivity, which is associated with the easy replacement of the diene or triene ligands by substrate molecules, has led to their being named "naked" nickel or "ligand-free" nickel compounds.<sup>6,7</sup> The impact of this discovery can be judged by the appearance in the last 20 years of several thousand primary publications on organonickel chemistry.<sup>3</sup>

Obviously, from the foregoing remarks, "ligand-free" Pt(0) compounds [P(olefin)<sub>n</sub>] would be very desirable reagents for use in a variety of syntheses. That such compounds could exist was demonstrated by Müller and Göser,<sup>8</sup> who prepared [Pt(cod)<sub>2</sub>] for the first time.

(1) U. Belluco, "Organometallic and Co-ordination Chemistry of Platinum", Academic Press, London, 1974.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); J. Chatt, *Record Chem. Prog.*, **21**, 147 (1960); J. Chatt, *Accad. Naz. Lincei*, **121** (1961).

(3) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, 2, Academic Press, New York, 1974, and 1975.

(4) E. P. Kundig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 7234 (1973).

(5) G. Wilke, *Angew. Chem.*, **72**, 581 (1960); B. Bogdanović, M. Kröner, and G. Wilke, *Liebigs Ann. Chem.*, **699**, 1 (1966).

(6) G. Wilke, *J. Organomet. Chem.*, **200**, 349 (1980).

(7) See p 134 of ref 3, Vol. 2.

Gordon Stone was born in Exeter, England, and educated at Cambridge University. After appointments at the Universities of Southern California, Harvard, and London, he became Professor of Inorganic Chemistry at Bristol University. He is a Fellow of the Royal Society, and is currently President of the Dalton Division of the Royal Society of Chemistry.

Their method involved reacting  $[\text{PtCl}_2(\text{cod})]$  with isopropylmagnesium halide at low temperatures so as to obtain  $[\text{Pt-}i\text{-Pr}_2(\text{cod})]$  (40% yield). The latter compound was irradiated with UV light in the presence of cod, whereupon it underwent a reductive elimination reaction to give  $[\text{Pt}(\text{cod})_2]$  (22% yield).

Our attention was drawn to  $[\text{Pt}(\text{cod})_2]$  following a long-standing interest in Malatesta's<sup>9</sup> compounds  $[\text{Pt}(\text{PR}_3)_n]$  ( $n = 3$  or  $4$ ) which we had employed in syntheses to obtain species with carbon-platinum bonds or bonds between platinum and other metals of subgroup 8.<sup>10</sup> The Malatesta-type precursors, however, suffer from the disadvantage of possessing  $\text{PR}_3$  ligands which block coordination sites on platinum. Moreover, although in solution these complexes dissociate  $\text{PR}_3$  groups to some extent, the latter when released often enter into side reactions, thereby reducing the yield of desired platinum compound.<sup>11</sup> Hence a new synthesis of the compound  $[\text{Pt}(\text{cod})_2]$  was required so that it could be available in quantity; the earlier method<sup>8</sup> gave rise to low and erratic yields.

### Ligand-Free Platinum Compounds: Synthesis and Structure

Bis(1,5-cyclooctadiene)platinum was prepared (~70% yield) by reducing  $[\text{PtCl}_2(\text{cod})]$  with the lithium salt of cyclooctatetraene (cot) in the presence of excess cod.<sup>12</sup> The  $\text{cot}^{2-}$  anion was chosen as the reducing agent in the expectation that upon its oxidation to cot the latter would not coordinate to Pt(O) in the presence of excess cod.<sup>13</sup> The compound  $[\text{Pt}(\text{cod})_2]$  is appreciably more oxidatively and thermally stable than its nickel analogue, and the dry solid may be handled in air. The molecular structure has been determined by an x-ray diffraction study.<sup>14</sup> As with the nickel analogue,<sup>3</sup> the metal atom is in an essentially tetrahedral environment as a consequence of the disposition of the four C=C bonds of the two cod ligands. The angle of "bite" of the chelate rings is, however, only  $86^\circ$  rather than  $110^\circ$  for the "tetrahedral"  $\text{Pt}^0(\text{d}^{10})$ , and this may in part account for the displacement of these groups by ethylene to give  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  and the ready loss of one or both cod groups in reactions to be described.

Formation of the 16-electron complex  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  by treating the 18-electron compound  $[\text{Pt}(\text{cod})_2]$  with excess  $\text{C}_2\text{H}_4$  proved to be a singularly important result. The physical and chemical properties of  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  are

(8) J. Müller and P. Göser, *Angew. Chem., Int. Ed. Engl.*, **6**, 364 (1967).

(9) L. Malatesta and S. Cenini, "Zerovalent Compounds of Metals", Academic Press, London, 1974.

(10) The reactions included those involving (a) oxidative insertion of platinum into the C-I bonds of perfluoroalkyl iodides [D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, 164 (1968)], (b) formation of adducts with  $\text{C}_2\text{F}_4$ ,  $(\text{CF}_3)_2\text{CO}$ , etc. [M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone *ibid.*, 2525 (1968); B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *ibid.*, 167 (1968)], (c) oxidative insertion of platinum into carborane polyhedra [M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc. Dalton Trans.*, 1979 (1975)], and (d) formation of heteronuclear transition-metal cluster carbonyl complexes [M. I. Bruce, G. Shaw, and F. G. A. Stone, *ibid.*, 1082, 1781 (1972)]. For reviews, see F. G. A. Stone, *Pure Appl. Chem.*, **30**, 551 (1972); *J. Organomet. Chem.*, **100**, 257 (1975).

(11) The reaction between  $[\text{Os}_3(\text{CO})_{12}]$  and  $[\text{Pt}(\text{PMePh}_2)_4]$  gives mainly  $[\text{Os}_3(\text{CO})_{12-n}(\text{PMePh}_2)_n]$  and no complexes containing Os-Pt bonds.<sup>10a</sup>

(12) M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 271 (1977); J. L. Spencer, *Inorg. Synth.*, **19**, 213 (1979).

(13) Cobaltocene, which is readily oxidized to  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ , has also been used as a reducing agent in this synthesis [G. E. Herberich and B. Hessner, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **34B**, 638 (1979)].

(14) J. A. K. Howard, to be published.

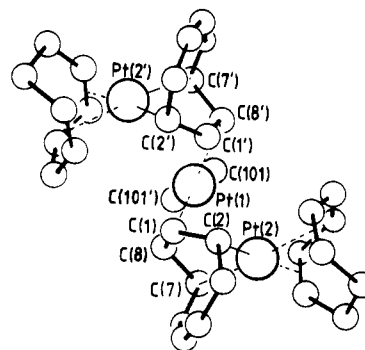


Figure 1. The molecule  $[\text{Pt}_3(\text{C}_2\text{H}_4)_3(\mu\text{-C}_8\text{H}_8)_2(\text{C}_8\text{H}_{12})_2]$ . The Pt-Pt separations are 3.166 (1) Å. Reproduced with permission from ref 19. Copyright 1981, The Royal Society of Chemistry.

akin to those of  $[\text{Ni}(\text{CO})_4]$  in the sense that the platinum compound is volatile and readily loses its ligands. Tris(ethylene)platinum is a white crystalline compound, stable for several hours at  $20^\circ\text{C}$  under 1 atm of ethylene, and may be kept for many weeks at  $-20^\circ\text{C}$ . In the absence of ethylene, decomposition to metallic platinum occurs in minutes at room temperature.<sup>12,15</sup> Other tris(olefin)platinum(0) complexes (where olefin represents a strained olefin such as bicyclo[2.2.1]-heptene, dicyclopentadiene, or *trans*-cyclooctene) may be similarly obtained by direct displacement of cod from  $[\text{Pt}(\text{cod})_2]$ .

The  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  molecule (neutron diffraction<sup>16</sup>) has a coplanar arrangement for the platinum and the six carbon atoms. This is in accord with the prediction<sup>17</sup> that as a consequence of the synergic effect of  $\sigma$  and  $\pi$  bonding, the trigonal "planar" structure would be preferred over the alternative trigonal "upright" structure for the  $\text{C}_2\text{H}_4$  ligands. The ligated carbon atoms in  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{F}_4)]$ <sup>18</sup> and  $[\text{Pt}(\text{bicyclo}[2.2.1]\text{-heptene})_3]$ <sup>12</sup> are also coplanar with the metal atoms.

The reaction of  $[\text{Pt}(\text{cod})_2]$  with  $\text{C}_2\text{H}_4$  which gives  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  can be reversed by treating the latter with cod. Although  $[\text{Pt}(\text{cod})_2]$  is isolated from a synthesis which liberates cot, it is likely that intermediates in which both cot and cod ligands are bonded to platinum are involved. That cod, cot, and  $\text{C}_2\text{H}_4$  have similar affinities for platinum has been demonstrated by the synthesis of  $[\text{Pt}_3(\text{C}_2\text{H}_4)(\text{cod})_2(\text{cot})_2]$  by reacting an ethylene-saturated diethyl ether solution of  $[\text{Pt}(\text{cod})_2]$  with cyclooctatetraene.<sup>19</sup> The molecular structure (Figure 1) is one in which two cod ligands, in their usual tublike configuration, are  $\eta^4$ -coordinated to Pt(2) and Pt(2'), while the Pt(1)-Pt(2) and Pt(1)-Pt(2') are bridged by two cot ligands which employ four adjacent carbon atoms for bonding to the metal atoms. Of these carbon atoms, the central pair [C(1), C(8) and C(1'), C(8')] form a C=C bond  $\eta^2$ -coordinated to Pt(1) while the outer two [C(2), C(7) and C(2'), C(7')] are attached to Pt(2) [or Pt(2')] via  $\sigma$  bonds. The central metal atom Pt(1) is also bonded to an  $\text{C}_2\text{H}_4$  molecule [C(101), C(101')] so that it is in a distorted trigonal configuration.

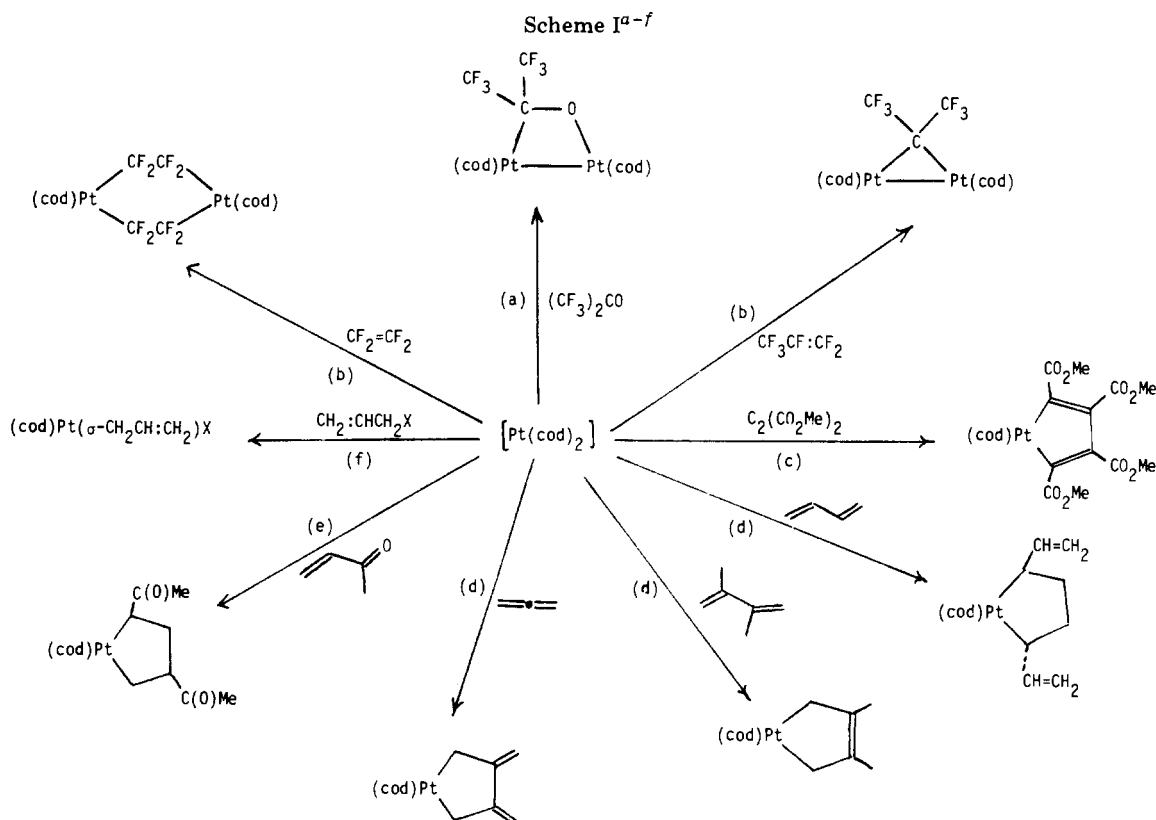
(15) Fortunately tris(ethylene)platinum is apparently thermally more stable than  $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ , which decomposes above  $0^\circ\text{C}$  [K. Fischer, K. Jonas, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **12**, 565 (1973)].

(16) J. A. K. Howard, S. A. Mason, and J. L. Spencer, to be published.

(17) N. Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1974).

(18) M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 449 (1975).

(19) N. M. Boag, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1051 (1981).



<sup>a</sup> M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 298 (1977). <sup>b</sup> M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1010 (1977). <sup>c</sup> N. M. Boag, G. H. M. Dias, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *ibid.*, 1981 (1981). <sup>d</sup> G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1839 (1978). <sup>e</sup> M. Green, J. A. K. Howard, P. Mitprachachon, M. Pfeffer, J. L. Spencer, F. G. A. Stone, and P. Woodward, *ibid.*, 306 (1979). <sup>f</sup> N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1200 (1980).

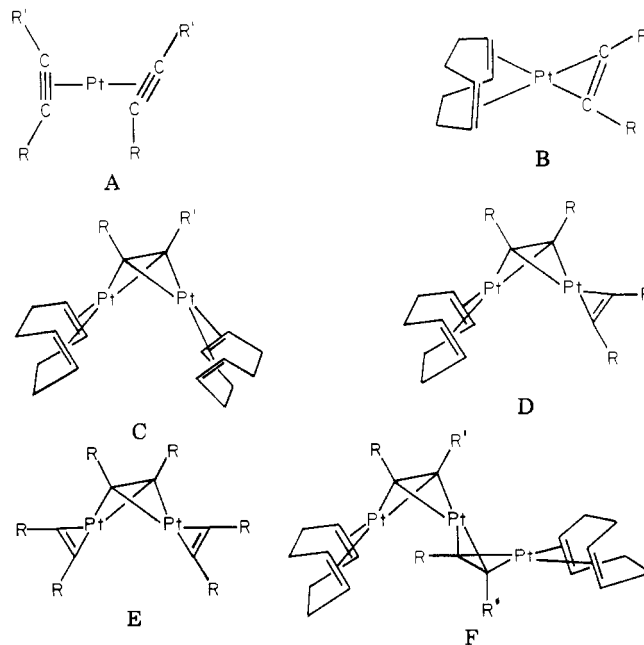
This is in contrast to Pt(2) and Pt(2') which have essentially square-planar environments comprised of two  $\sigma$  bonds from one cod ligand and the two C=C bonds of a cod ring. The Pt-Pt separations (Figure 1) are too long for any significant direct metal-metal bonding.

### Reactivity Patterns for Bis(1,5-cyclooctadiene)platinum and Tris(ethylene)platinum

As anticipated, by analogy with the "ligand-free" nickel species,<sup>3</sup> the compounds [Pt(cod)<sub>2</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>] have an extensive chemistry. Most reactions of [Pt(cod)<sub>2</sub>] lead to displacement of one of the cod groups, and the versatility of its reactions with organic molecules is illustrated (Scheme I). Both [Pt(cod)<sub>2</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>] react with alkynes, the nature of the products (A-F) depending on the alkyne used and the stoichiometry employed (Chart I).

Several bis(alkyne)platinum complexes [Pt(R<sup>1</sup>C<sub>2</sub>R<sup>2</sup>)<sub>2</sub>] have been prepared from [Pt(cod)<sub>2</sub>] and an excess of the alkyne, and other members of this same class have been obtained from [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>]. The molecular structure of the complex from diphenylacetylene (Figure 2)<sup>20</sup> reveals for the metal a distorted tetrahedral configuration, with the angle between the two Pt-C-C planes being 82°. This compound forms from [Pt(cod)<sub>2</sub>] via the intermediacy of [Pt(PhC<sub>2</sub>Ph)(cod)], which has also been characterized, as have several other alkyne

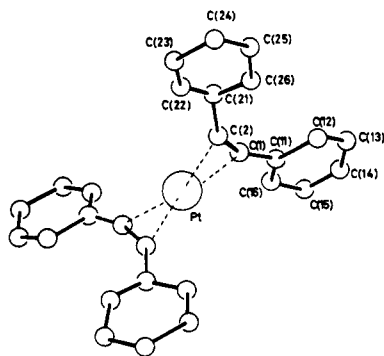
Chart I  
Molecular Structures of Some Alkyne-Platinum Complexes Obtained from [Pt(cod)<sub>2</sub>] or [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>]



complexes of this class. Several di- and triplatinum-alkyne complexes have been isolated.<sup>21,22</sup> Thus [Pt-

(20) N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2170 (1980).

(21) N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, M. D. O. Thomas, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2182 (1980).



**Figure 2.** Molecular structure of  $[\text{Pt}(\text{PhC}_2\text{Ph})_2]$ . Reproduced with permission from ref 20. Copyright 1980, The Royal Society of Chemistry.

$(\text{C}_2\text{H}_4)_3$  and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  afford  $[\text{Pt}_2(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)(\text{Me}_3\text{SiC}_2\text{SiMe}_3)_2]$ , of structural type E, while  $\text{PhC}\equiv\text{CSiMe}_3$  and  $[\text{Pt}(\text{cod})_2]$  give  $[\text{Pt}_3(\mu\text{-PhC}_2\text{SiMe}_3)_2(\text{cod})_2]$ , of type F. There is no evidence for any direct metal-metal bonding in species of type C-F,<sup>21,22</sup> the platinum-platinum separations being determined by the geometrical requirements of the transversely bridging alkyne groups which employ their orthogonal  $\pi$  orbitals to bond to two metal atoms. However, in other diplatinum-alkyne complexes derived from  $[\text{Pt}(\text{cod})_2]$  the alkyne ligand adopts a  $\mu\text{-}\eta^1$  bridging mode affording a diplatina-cyclobutene structure, rather than the diplatina-tetrahedrane configurations in C-F. Thus there are two isomers of  $[\text{Pt}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{cod})_2]$ , one of structural type C and the other with a  $\text{Pt}-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{Pt}$  arrangement. The metal-metal bond present in the latter species may be protonated, giving a cationic  $\text{Pt}(\mu\text{-H})\text{Pt}$  hydride, which rearranges to yield a diplatinum bridged-vinyl compound,  $[\text{Pt}_2(\mu\text{-}\eta^1, \eta^2\text{-C}(\text{CF}_3)=\text{CH}(\text{CF}_3))(\text{cod})_2]$ .<sup>23</sup>

Reactions between  $[\text{Pt}(\text{cod})_2]$  or  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  and tertiary phosphines or isocyanides are important since the products are themselves very useful reagents for further syntheses. *tert*-Butyl isocyanide reacts with  $[\text{Pt}(\text{cod})_2]$  to give  $[\text{Pt}_3(\mu\text{-CNBu-}t)_3(\text{CNBu-}t)_3]$  which has three terminal and three bridging  $\text{CNBu-}t$  ligands.<sup>24</sup> This compound is a ready source of  $\text{Pt}(\text{CNBu-}t)_2$  fragments in synthesis.

Treatment of  $[\text{Pt}(\text{cod})_2]$  or  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  with sterically demanding  $\text{PR}_3$  molecules [e.g.,  $\text{P}(\text{C}_6\text{H}_{11})_3$ ,  $\text{PBu-}t_2\text{Me}$ ] affords the 14-electron platinum complexes  $[\text{Pt}(\text{PR}_3)_2]$ .<sup>25,26</sup> More important are reactions of the ligand-free platinum compounds with tertiary phosphines having less bulky substituent groups, since in this manner a range of useful complexes,  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ , can readily be obtained. The former species are prepared by adding 2 mol of  $\text{PR}_3$  to an ethylene-saturated solution of  $[\text{Pt}(\text{cod})_2]$  at  $\sim 0^\circ\text{C}$ .

The latter compounds can be isolated by adding 1 equiv of  $\text{PR}_3$  to an in situ generated solution of  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ .<sup>27</sup> Usually the complexes  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  are not isolated, but are employed immediately as reagents in syntheses.

A few compounds of type  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  have long been known,<sup>1,28</sup> but species having a variety of different alkyl groups on the phosphorus atoms have not hitherto been readily accessible. The compounds  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  have trigonal structures, with the Pt, P, and C atoms of the  $\text{C}_2\text{H}_4$  ligands coplanar.<sup>27,29</sup> The molecules undergo dynamic behavior in solution, the  $\text{C}_2\text{H}_4$  ligands rotating about an axis through the metal atom and the midpoints of the  $\text{C}=\text{C}$  bonds. From variable temperature  $^1\text{H}$  NMR data the activation energies ( $\Delta G_{T_c}^\ddagger$ ) for this process have been estimated at from 54 to 43  $\text{kJ mol}^{-1}$ , depending on the nature of the  $\text{PR}_3$  groups.<sup>27</sup>

### (Tertiary phosphine)(ethylene)platinum Compounds in Synthesis

The compounds  $[\text{Pt}(\text{cod})_2]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  provide the chemist with ready sources of either  $\text{Pt}(\text{cod})$  groups or naked platinum. The aforementioned (tertiary phosphine)(ethylene)platinum complexes add to the range of reactive species for synthesis work since via loss of ethylene they are sources either of  $\text{Pt}(\text{PR}_3)$  or  $\text{Pt}(\text{PR}_3)_2$  groups.

Representative compounds prepared from  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  are shown in Scheme II, where emphasis has been given to reactions with organosilicon or -tin molecules, since complexes with bonds between platinum and silicon or tin are readily obtained via these reagents. Moreover, several of these products have interesting properties.<sup>30</sup> Thus the compounds  $[\text{Pt}(\mu\text{-H})(\text{SiR}'_3)(\text{PR}_3)_2]$  are very efficient catalysts for the hydrosilylation of alkenes, alkynes, or  $\alpha, \beta$ -unsaturated aldehydes and ketones.<sup>31</sup> An interesting feature of the  $^1\text{H}$  NMR spectra of the compounds  $[\text{Pt}(\mu\text{-H})(\text{SiR}'_3)(\text{PR}_3)_2]$  and  $[\text{PtH}(\mu\text{-SiR}'_2)(\text{PR}_3)_2]$  is that the platinum-bonded hydrido ligands show resonances at relatively low field ( $\delta \sim 2\text{--}3$ ). From this and other properties some interaction in solution of the type  $\text{Pt}(\mu\text{-H})\text{Si}$  has been postulated.<sup>30</sup>

The most interesting facet of the chemistry of the complexes  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ <sup>27,32</sup>

(27) N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1337 (1978).

(28) The complex  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  was first obtained by ethylene displacement of  $\text{O}_2$  from  $[\text{PtO}_2(\text{PPh}_3)_2]$ , the latter being prepared by reacting oxygen with  $[\text{Pt}(\text{PPh}_3)_4]$  [C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **90**, 1464 (1968)].

(29) A single-crystal X-ray diffraction study has confirmed this structure for  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\text{P}(\text{C}_6\text{H}_{11})_3]$  (J. A. K. Howard, P. Mitrprachachon, and P. Woodward, unpublished results).

(30) M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 801 (1978); M. Auburn, M. Ciriano, J. A. K. Howard, M. Murray, N. J. Pugh, J. L. Spencer, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 659 (1980).

(31) M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1519, 1525 (1977); A. P. Barlow, N. M. Boag, and F. G. A. Stone, *J. Organomet. Chem.*, **191**, 39 (1980).

(32) Although  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PEt}_3)]$  can be prepared,<sup>27</sup> treatment of  $[\text{Pt}(\text{cod})_2]$  with 2 equiv. of triethylphosphine in the absence of  $\text{C}_2\text{H}_4$  affords a compound formulated as  $[\text{Pt}_2(\mu\text{-cod})(\text{PEt}_3)_4]$ . The latter is a useful reagent for synthesizing platinacarboranes via direct oxidative insertion of  $\text{Pt}(\text{PEt}_3)_2$  groups into carboranes [G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, and G. Siwapanoyos, *J. Chem. Soc., Dalton Trans.*, 1687 (1979)]. Thus  $2,3\text{-C}_2\text{B}_4\text{H}_8$  and  $[\text{Pt}_2(\mu\text{-cod})(\text{PEt}_3)_4]$  yield  $[\text{nido-}\mu_{4,5}\text{-trans-(Et}_3\text{P)}_2\text{Pt(H)-}\mu_{6,6}\text{-H-2,3-C}_2\text{B}_4\text{H}_8]$ , which on pyrolysis affords  $[\text{closo-1,1-(Et}_3\text{P)}_2\text{-1,2,4-PtC}_2\text{B}_4\text{H}_8]$  [G. K. Barker, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1186 (1980)].

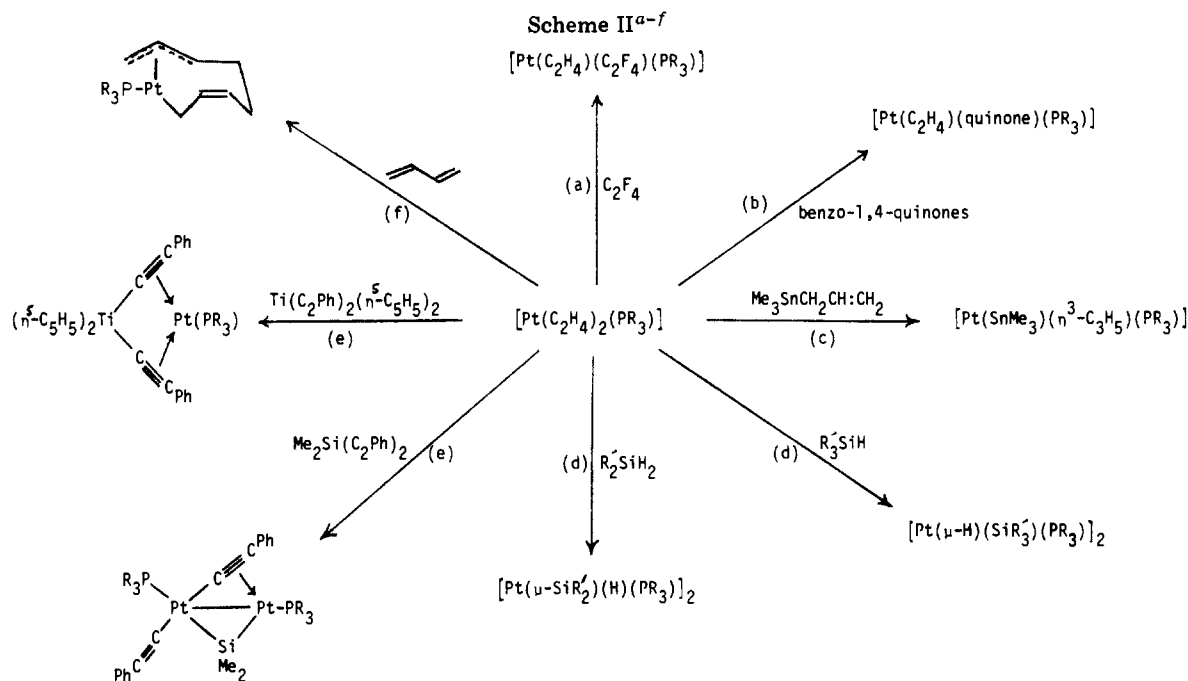
(22) N. M. Boag, M. Green, J. A. K. Howard, F. G. A. Stone, and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 862 (1981).

(23) N. M. Boag, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1281 (1980).

(24) M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1509 (1977).

(25) J. Forniés, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).

(26) These compounds have also been prepared by others [A. Immirzi, A. Musco, P. Zambelli, and G. Carturan, *Inorg. Chim. Acta*, **13**, L13 (1975); S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1977)] by alternative routes following our initial communication [M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 3 (1975)].



<sup>a</sup> Reference 27. <sup>b</sup> M. J. Chetcuti, J. A. Herbert, J. A. K. Howard, M. Pfeffer, J. L. Spencer, F. G. A. Stone, and P. Woodward, *J. Chem. Soc. Dalton Trans.*, 284 (1981). <sup>c</sup> A. Christofides, M. Ciriano, J. L. Spencer, and F. G. A. Stone, *J. Organomet. Chem.*, 178, 273 (1979). <sup>d</sup> Reference 30. <sup>e</sup> M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, and H. Wadepl, *J. Chem. Soc., Dalton Trans.*, 1749 (1979). <sup>f</sup> G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1839 (1978).

is their use in preparing compounds with bonds between platinum and other metals,<sup>33</sup> now briefly described.

### Abstraction of CO Ligands

We referred earlier<sup>10d</sup> to reactions between Malatesta's compounds, [Pt(PR<sub>3</sub>)<sub>4</sub>], and the carbonyls of Fe, Ru, and Os. Although the first examples of platinum-containing "mixed-metal" carbonyl complexes were obtained in this manner, e.g., [Pt<sub>2</sub>Ru(CO)<sub>5</sub>(PMePh<sub>2</sub>)<sub>3</sub>], side reactions afforded tertiary phosphine derivatives of Fe, Ru, or Os carbonyls,<sup>11</sup> due to the presence of free PR<sub>3</sub> groups released from the [Pt(PR<sub>3</sub>)<sub>4</sub>] species. This difficulty cannot arise in reactions using [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)] as the platinum source since these molecules do not dissociate PR<sub>3</sub> groups. Moreover, these platinum complexes are so reactive toward CO<sup>34</sup> that they will abstract this group from coordinatively saturated carbonyl compounds, a useful property for use in synthesizing complexes with heteronuclear metal-metal bonds containing Pt(CO)(PR<sub>3</sub>) groups. For example, [H<sub>2</sub>Os(CO)<sub>4</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] react at room temperature in pentane to give the diosmium-diplatinum complex [Os<sub>2</sub>Pt<sub>2</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)<sub>2</sub>],<sup>35</sup> a compound with a "butterfly" configuration for the metal atom framework. A similar geometry<sup>36</sup> is adopted by the metal atoms in the anion [Fe<sub>2</sub>Pt<sub>2</sub>(μ-H)(μ-CO)<sub>3</sub>(CO)<sub>5</sub>-

(PPh<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, prepared by reacting [HFe<sub>2</sub>(CO)<sub>8</sub>]<sup>-</sup> with [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].<sup>35</sup> Whatever the detailed mechanisms of these syntheses, the net effect is transfer of CO to platinum, yielding a Pt(CO)(PR<sub>3</sub>) group which, in combination with the coordinatively unsaturated metal carbonyl species so generated, gives a heteronuclear cluster as the end product. The molecules [Pt(cod)<sub>2</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>] should similarly form bonds between platinum and other transition metals.<sup>37</sup> Thus we have prepared [PtRh<sub>2</sub>(μ<sub>3</sub>-CO)<sub>2</sub>(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] in high yield from [Pt(cod)<sub>2</sub>] and [Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)].<sup>38</sup> Presumably the latter compound transfers CO ligands to platinum, perhaps affording [Rh<sub>2</sub>(μ-CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] as an intermediate, the Rh=Rh bond of which then adds Pt(CO)<sub>2</sub> (see later).

It seems likely that in these reactions the platinum nucleophiles initially attack the M-CO bonds to give transient M(μ-CO)Pt species, thereby providing a mechanism for CO migration and formation of an M-Pt-CO group. Interestingly, reactions occur between [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and the compounds [M(CO)<sub>2</sub>(CS)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (M = Mn or Re) to give complexes [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(OC)<sub>2</sub>M(μ-CS)Pt(PMe<sub>2</sub>Ph)<sub>2</sub>] with bridging CS ligands.<sup>39</sup> The Pt(PMe<sub>2</sub>Ph)<sub>2</sub> fragment evidently attacks the softer M-CS group in preference to the M-CO.

### Addition to Metal-Carbon Multiple Bonds

A novel reaction between CF<sub>3</sub>CF=CF<sub>2</sub> and [Pt(cod)<sub>2</sub>], which gave [(cod)Pt(μ-C(CF<sub>3</sub>)<sub>2</sub>)Pt(cod)]

(33) F. G. A. Stone, *Inorg. Chim. Acta*, 50, 33 (1981).

(34) Traces of CO react to give triplatinum compounds [Pt<sub>3</sub>(μ-CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>].

(35) L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1134, 1274 (1981).

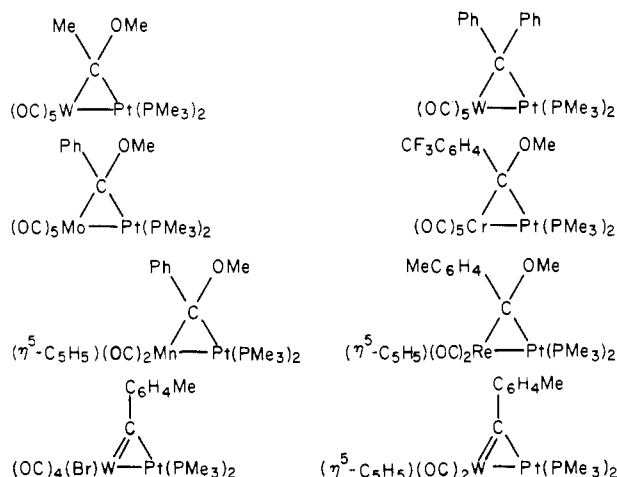
(36) It is interesting that these Os<sub>2</sub>Pt<sub>2</sub> and Fe<sub>2</sub>Pt<sub>2</sub> clusters with 58 valence electrons and 5 skeletal bond pairs adopt the geometry expected for transition-metal clusters with 62 cluster valence electrons and 7 skeletal bond pairs. This behavior is typical for platinum, leading to deviations from the electron pair counting rules for clusters [J. Wade in "Transition Metal Clusters", B. F. G. Johnson, Ed., Wiley, New York, 1980, Chapter 3].

(37) Ligand-free complexes of other transition metals should react similarly with coordinatively saturated metal carbonyl compounds.

(38) G. N. Pain, to be published.

(39) J. C. Jeffery, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 243 (1981).

Scheme III



(Scheme I), pointed the way to a versatile method of forming heteronuclear metal-metal bonds. It seems probable that the reaction of  $\text{CF}_3\text{CF}=\text{CF}_2$  with  $[\text{Pt}(\text{cod})_2]$  involves an intermediate  $(\text{cod})\text{Pt}=\text{C}(\text{CF}_3)_2$   $[(\text{cod})\text{Pt}^+-\text{C}(\text{CF}_3)_2^-]$ , the  $\text{Pt}\rightarrow\text{C}$  bond of which is subsequently attacked by  $\text{Pt}(\text{cod})$  to give the final product. It thus became apparent that mononuclear metal complexes having metal-carbon multiple bonds (i.e., carbene or carbyne complexes) should add  $\text{PtL}_2$  fragments to give dimetal compounds with bridging alkylidene and alkylidyne ligands. This simple idea, amply confirmed by experiment, has opened up a vast new area for research with the synthesis of large numbers of compounds.<sup>40,41</sup> A few such complexes are shown in Scheme III, all of which are obtained in good yield by reacting  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  (prepared in situ from  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ ) with the appropriate metal-carbene or -carbyne compound.

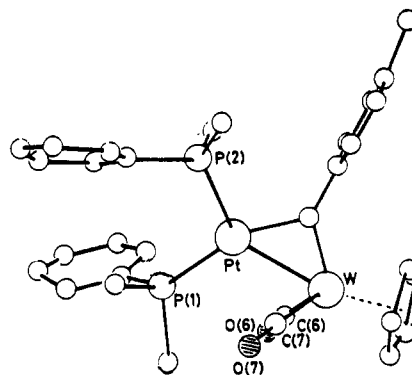
In the complexes having a dimetallacyclopropane framework the alkylidene groups in general do not symmetrically bridge the metal-metal bonds.<sup>40b,f</sup> Indeed, in some instances a complete transfer of the alkylidene group has been observed, so that it becomes terminally bonded to the platinum.<sup>42</sup> Moreover, the degree to which the alkylidene group migrates from one metal center to another depends on the nature of the other ligands present in the molecules. This migratory behavior is reminiscent of the properties of CO ligands in dimetal carbonyls<sup>43</sup> and will be manifested in the chemistry of complexes such as those shown in Scheme III. Thus under relatively mild conditions (toluene, 80 °C),  $[\text{CrPt}\{\mu\text{-C}(\text{OMe})\text{Ph}\}(\text{CO})_5(\text{PMe}_3)_2]$  affords the triplatinum compounds  $[\text{Pt}\{\mu\text{-C}(\text{OMe})\text{Ph}\}(\text{PMe}_3)_3]$  and  $[\text{Pt}_3(\mu\text{-CO})\{\mu\text{-C}(\text{OMe})\text{Ph}\}_2(\text{PMe}_3)_3]$ .<sup>40e</sup>

(40) (a) T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 42 (1979); T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *ibid.*, 43, 45 (1979); (b) T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1593 (1980); (c) M. Berry, J. A. K. Howard, and F. G. A. Stone, *ibid.*, 1601 (1980); (d) T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *ibid.*, 1609 (1980); (e) T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *ibid.*, 1615 (1980); (f) J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone, and P. Woodward, *ibid.*, 743 (1981); J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *ibid.*, 751 (1981).

(41) The method of synthesis is not limited to platinum, since in principle any "ligand-free" or "ligand-stabilized" nucleophilic metal fragment will add to  $\text{M}=\text{C}$  or  $\text{M}\equiv\text{C}$  groups (see ref 40c).

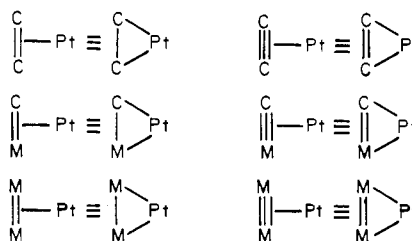
(42) M. Berry, J. Martin-Gil, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1625 (1980).

(43) F. A. Cotton, *Prog. Inorg. Chem.*, 21, 1 (1976).



**Figure 3.** Structure of the compound  $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Pt}(\text{PMe}_2\text{Ph})_2]$ . The plane defined by the carbon atoms of the alkylidene ligand is at  $88^\circ$  to the  $\text{Pt}(\mu\text{-C})\text{W}$  plane. Reproduced with permission from ref 40d. Copyright 1980, The Royal Society of Chemistry.

Scheme IV



The structure of the product from the reaction between  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$  and  $[\text{W}=\text{CC}_6\text{H}_4\text{Me-4}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  is shown in Figure 3.<sup>40d</sup> The  $\text{W}-\mu\text{-C}$  distance [1.967 (6) Å] corresponds fairly closely to that expected for a  $\text{W}=\text{C}$  bond<sup>44</sup> and is somewhat longer than the  $\text{W}\equiv\text{C}$  bond [1.82 (2) Å] in the precursor  $[\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ .<sup>45</sup> A further interesting structural feature is the disposition of the CO ligands which, although deviating only slightly ( $\sim 6^\circ$ ) from forming linear  $\text{W}-\text{C}-\text{O}$  groups, lie back over the top of the  $\text{Pt}-\text{W}$  bond ( $\angle\text{Pt}-\text{W}-\text{CO}$  67.4 and 72.0°), suggesting some interaction between the CO groups and the platinum, an idea supported by the IR data with  $\nu_{\text{CO}}$  (max) at the low frequencies of 1898 and 1818  $\text{cm}^{-1}$ . Evidently there is considerable electron delocalization within the dimetallacyclopropane ring system, with the CO ligands playing a noninnocent role.<sup>46</sup> The reactivity of the dimetallacyclopropane rings in this and other compounds of this class is currently being investigated, since clearly these formally unsaturated species should have an extensive chemistry. The most exciting discovery so far is the ability of the rings to add other metal-ligand fragments to yield trimetallic complexes with triply bridging alkylidyne ligands. For example,  $[\text{PtW}(\mu_2\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_2(\text{PET}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$  reacts with  $[\text{Fe}_2(\text{CO})_9]$  in tetrahydrofuran at room temperature to afford  $[\text{Fe}(\text{CO})_4(\text{PET}_3)]$  and  $[\text{FePtW}(\mu_3\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_6(\text{PET}_3)(\eta^5\text{-C}_5\text{H}_5)]$ .<sup>47</sup> This method of obtaining

(44) In the mononuclear complex  $[\text{W}=\text{CPh}_2(\text{CO})_6]$ , the  $\text{W}=\text{C}$  distance is 2.14 (2) Å [C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, 99, 2127 (1977)].

(45) E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 110, 3397 (1977).

(46) E. D. Jemmis, A. R. Pinhas, and R. Hoffmann, *J. Am. Chem. Soc.*, 102, 2576 (1980).

(47) M. J. Chetcuti, M. Green, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, S. J. Porter, F. G. A. Stone, A. A. Wilson, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1057 (1980).

trimetallic clusters with three different transition elements is of wide applicability.<sup>47,48</sup> An interesting family of structurally related homonuclear trimetal complexes,  $[\text{Co}_3(\mu\text{-CR})(\text{CO})_9]$ , has been known for many years.<sup>49</sup>

### Isolobal Relationships

By now the reader should have recognized a striking analogy between the chemical reactivity patterns of  $\text{PtL}_2(\text{d}^{10})$  fragments toward the groups  $\text{C}=\text{C}$  and  $\text{M}=\text{C}$  and the groups  $\text{C}=\text{C}$  and  $\text{M}=\text{C}$  (Scheme IV). These reactivity patterns can be understood in terms of various isolobal relationships, a concept developed in elegant papers by R. Hoffmann and co-workers.<sup>50</sup> For the group  $\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ , the number, symmetry properties, extent in space, and energy of the frontier orbitals are similar to those of  $\text{RC}\equiv$ , and hence with the benefit of hindsight it is not surprising that the compound  $[\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  exists, or that it forms an adduct with  $\text{Pt}(\text{PR}_3)_2$ , as do many alkynes.<sup>1</sup> However, once the isolobal relationships<sup>50,51</sup> are recognized, the preparative chemist can attempt some designed syntheses. This is well illustrated by the following example. We referred earlier to the compounds  $[\text{Pt}(\text{alkyne})_2]$  (Figure 2). Because of the valence orbital similarities between  $\text{RC}\equiv\text{CR}$  and  $[\text{RC}\equiv\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ , it should be possible to obtain novel compounds in which a naked platinum atom is sandwiched between two metal-carbyne fragments. This has been accomplished by reacting  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  with 2 equiv of  $[\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  to give  $[\text{Pt}\{\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]$  in 75% yield.<sup>52,53</sup>

### Additions to Metal-Metal Multiple Bonds.

The logical extension of adding  $\text{PtL}_2$  fragments to complexes containing  $\text{M}=\text{C}$  or  $\text{M}\equiv\text{C}$  bonds is addition of these platinum species to compounds which formally contain multiple metal-metal bonds (Scheme IV). However, organometallic compounds with  $\text{M}=\text{M}$  or  $\text{M}\equiv\text{M}$  bonds also have bridging ligands (e.g., CO or H), raising the possibility that the electronic structures of these molecules do not involve direct metal-metal

(48) Thus,  $[\text{FeRhW}(\mu_3\text{-CC}_6\text{H}_4\text{Me})(\mu_2\text{-CO})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_9\text{H}_7)]$  has been obtained in a two-stage synthesis from  $[\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ . The latter is first reacted with  $[\text{Rh}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)]$  to give  $[\text{RhW}(\mu_2\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_9\text{H}_7)]$ , which on treatment with  $[\text{Fe}_2(\text{CO})_9]$  affords the  $\text{FeRhW}(\mu_3\text{-CR})$  species in 60% yield.<sup>47</sup>

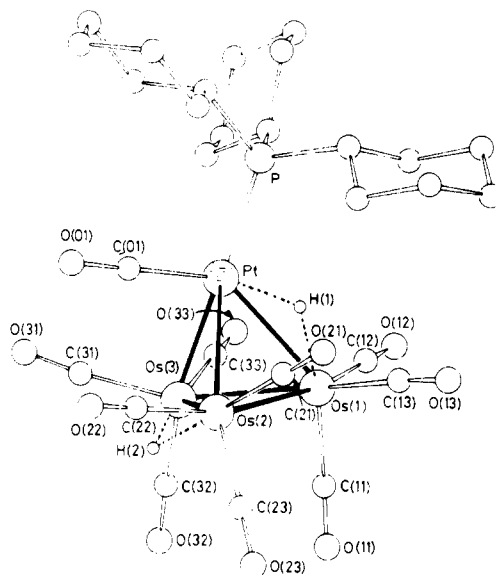
(49) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 98 (1976).

(50) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *ibid.*, **15**, 1148 (1976); B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979).

(51) Pertaining to this Account, the most useful isolobal relationships are those of  $\text{CH}$  with  $\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$  or  $\text{Co}(\text{CO})_3$ ,  $\text{CH}_2$  with  $\text{FeL}_4$  or  $\text{PtL}_2$ , and  $\text{CH}_3$  with  $\text{M}(\text{CO})_5$ . Thus a molecule of the type  $(\text{OC})_5\text{M}(\mu\text{-CR}_2)\text{PtL}_2$  (scheme III) can be viewed like an  $n$ -propyl cation  $(\text{CH}_3^+)(\text{CH}_2)$ , with the latter having the nonclassical cyclic geometry rather than the open classical arrangement. As mentioned in the text, the  $\text{M}-\text{Pt}-\text{CR}_2$  systems have semibringing carbene ligands<sup>40b,f</sup> corresponding to partially open ring structures like the classical structure for the  $\text{C}_3\text{H}_7^+$  cation. Moreover, because of the asymmetry in the  $\text{M}(\mu\text{-CR}_2)\text{Pt}$  rings it is appropriate to regard the  $\text{M}(\text{CO})_5$  species in Scheme III as involving coordination of this fragment to  $\text{R}_2\text{C}=\text{PtL}_2$  moieties (R. Hoffmann, personal communication).

(52) T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 763 (1981).

(53) Another synthesis which follows from considering isolobal relationships is the near-quantitative reaction between  $[\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  and  $[\text{Co}_2(\text{CO})_8]$  to give  $[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ . This process<sup>51</sup> is analogous to the well-known addition of  $\text{RC}\equiv\text{CR}$  across the  $\text{Co}-\text{Co}$  bond of dicobalt octacarbonyl with release of two CO groups.



**Figure 4.** The molecular structure of the platinum triosmium complex  $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}[\text{P}(\text{cyclo-C}_8\text{H}_{11})_3]]$ . The location of the hydrido ligands is deduced from relative metal-metal bond lengths, widening of certain  $\text{Pt}-\text{Os}-\text{CO}$  and  $\text{Os}-\text{Os}-\text{CO}$  angles, residual electron densities, and calculation of potential energy minima. Reproduced with permission from ref 62. Copyright 1981, The Royal Society of Chemistry.

multiple bonds but rather highly delocalized bridge bonding, as occurs in diborane.<sup>46</sup> Irrespective of the solution of this unresolved problem, it is evident that several polynuclear transition-metal complexes do not follow the 18-electron rule and consequently have sites showing electrophilic activity toward donor substrates. Herein we mention some work with  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ ,  $[\text{Rh}_2(\mu\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ , and  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ , all compounds formally considered to possess  $\text{M}=\text{M}$  bonds.<sup>54</sup>

The compound  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ <sup>55</sup> reacts with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  to give two trimetal complexes,  $[\text{PtRe}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2]$  and  $[\text{PtRe}_2(\mu\text{-H})_2(\text{CO})_9(\text{PPh}_3)]$ .<sup>56</sup> An x-ray crystallographic study on the latter product revealed a triangular  $\text{PtRe}_2$  arrangement with one hydrido ligand bridging the  $\text{Re}-\text{Re}$  bond and the other a  $\text{Pt}-\text{Re}$  bond. The platinum atom is also bonded to CO and  $\text{PPh}_3$  ligands, while each rhenium atom carries four terminal CO groups.

The novel compound  $[\text{Rh}_2(\mu\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ <sup>57</sup> reacts with  $[\text{Pt}(\text{cod})_2]$  and with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  to give  $[\text{Rh}_2\text{Pt}(\mu_3\text{-CO})_2(\text{cod})(\eta^5\text{-C}_5\text{Me}_5)_2]$  and  $[\text{Rh}_2\text{Pt}(\mu_3\text{-CO})_2(\text{CO})(\text{PPh}_3)(\eta^5\text{-C}_5\text{Me}_5)_2]$ , respectively. The former is produced in quantitative yield but the latter, which contains the ubiquitous  $\text{Pt}(\text{CO})(\text{PPh}_3)$  group, is isolated from a complex mixture.<sup>58</sup> Both  $\text{Rh}_2\text{Pt}$  species contain

(54) A difficulty arises in studying reactions of  $\text{Pt}(\text{d}^{10})$  species with compounds containing  $\text{M}=\text{M}$  bonds because most such molecules have bulky bridging ligands, thereby inhibiting approach to the metal centers by low-valent metal entities. However, addition of  $[\text{Pt}(\text{PPh}_3)_4]$  to the  $\text{Mo}\equiv\text{Mo}$  bond of  $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2]$  to give  $[\text{Mo}_2\text{Pt}(\text{CO})_4(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)_2]$  has been reported by M. D. Curtis and R. J. Klinger [*J. Organomet. Chem.*, **161**, 23, (1978)], but unfortunately no firm characterization of the  $\text{Mo}_2\text{Pt}$  compound was accomplished.

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asymmetric triply bridging CO ligands, as previously found<sup>59</sup> in the anion  $[\text{Rh}_3(\mu_3\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]^-$ . The latter species, and the two  $\text{Rh}_2\text{Pt}$  compounds, can be regarded electronically as resulting from interaction between isolobal 14-electron fragments  $\text{Rh}(\text{CO})_2^-$  or  $\text{PtL}_2$  and an unsaturated  $\text{Rh}_2$  moiety.

The triosmium compound  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ <sup>60,61</sup> has two  $\text{Os}(\mu\text{-H})\text{Os}$  bridge bonds reminiscent of the B(H)B bonds in boranes. We referred earlier to the addition of  $\text{PtL}_2$  molecules to B(H)B bonds of *nido*-carboranes,<sup>32</sup> and it is therefore not surprising that  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  react readily with  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ .<sup>62</sup> The structure of the product from  $[\text{Pt}(\text{C}_2\text{H}_4)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  shows (Figure 4) that a CO ligand has migrated to platinum, and the molecule contains both  $\text{Os}(\mu\text{-H})\text{Os}$  and  $\text{Os}(\mu\text{-H})\text{Pt}$  bridges. The complex undergoes hydrido-ligand site exchange in solution, and with 58 cluster valence electrons displays an extensive chemistry involving reactions with donor ligands giving species  $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)\text{L}]$  ( $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ , or  $\text{AsPh}_3$ ) with a butterfly geometry for the  $\text{Os}_3\text{Pt}$  group.

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## Conclusion

In this account I have indicated some new vistas in organometallic chemistry revealed as a consequence of the availability of "ligand-free" organoplatinum compounds. These species are precursors not only to a multitude of compounds with platinum-carbon bonds but also to many new complexes with bonds between platinum and hydrogen, boron, silicon, tin, or various transition metals. The principles of synthesis employed, for example, CO abstraction from metal carbonyls, additions to carbon-metal bonds with bond orders greater than one, and complexation with metal-metal systems having electrophilic sites, are equally applicable to low-valent species of other transition metals. It may be in their role as models for organometallic syntheses that the platinum reagents herein described have their greatest potential, particularly if chemists take into account the guidelines provided by isolobal relationships.<sup>47,50,63</sup>

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