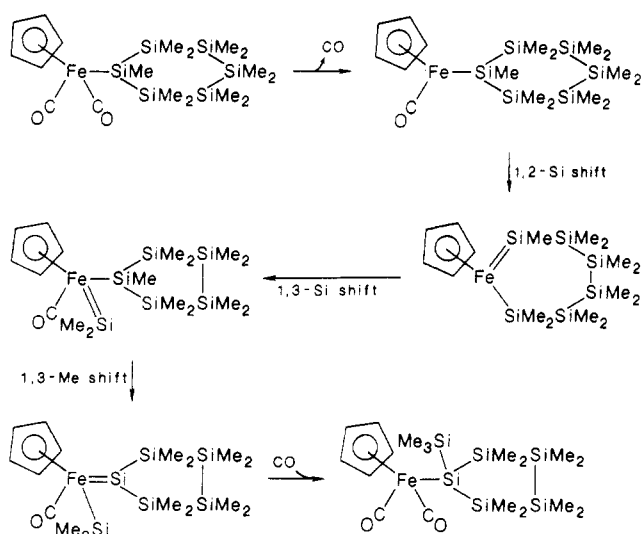
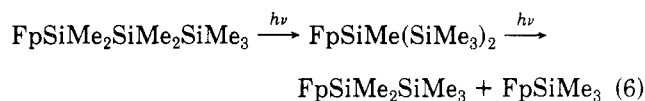


Scheme I



The key difference between the new rearrangements and the silylene expulsion reactions from the Fp-disilyl complexes is the lack of loss of Si fragments. If the above mechanism is operative, then recoordination of CO to silyl (silylene) Fp complexes where the silylene moiety contains silyl groups must cause re-formation of the Si-Si bond. Other mechanisms can be imagined, and our current studies are aimed at testing the various possibilities and discovering the extent to which other metals facilitate the skeletal rearrangements.

If the mechanism of the rearrangement of the linear Fp(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub> and Fp(SiMe<sub>2</sub>)<sub>5</sub>SiMe<sub>3</sub> follows closely that of Scheme I, the intermediacy of various branched chain isomers; e.g., FpSiMe(SiMe<sub>3</sub>)SiMe<sub>2</sub>SiMe<sub>3</sub> is to be expected. At the present time we have not observed such transient species during the reaction of the tetrasilyl and hexasilyl Fp complexes. However, related to our suggestion is the direct transient formation of FpSiMe(SiMe<sub>3</sub>)<sub>2</sub> upon irradiation of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>.<sup>20</sup> This rapidly further photodecomposes to form Fp-SiMe<sub>2</sub>SiMe<sub>3</sub> and Fp-SiMe<sub>3</sub> with ultimate formation of only Fp-SiMe<sub>3</sub>.



**Acknowledgment.** This research has been supported by the R.A. Welch Foundation, Houston, TX, and a Texas Advanced Technology Research Award. The support of the National Science Foundation through the establishment of a Minority Research Center of Excellence in Materials Science at U.T. El Paso is gratefully acknowledged.

(20) A concentrated solution of Fp-SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>, 80 mg in 400 mg of C<sub>6</sub>D<sub>6</sub>, was irradiated in a Pyrex NMR tube with a 450-W medium-pressure mercury lamp for 20 min at a distance of 10 cm. A <sup>13</sup>C NMR spectrum was recorded, and in addition to the three SiMe <sup>13</sup>C resonances of the starting material at -4.26, -1.02, and 5.04 ppm we observed approximately 30% conversion to FpSiMe(SiMe<sub>3</sub>)<sub>2</sub> as denoted by new resonances at -0.47 (SiMe) and 1.21 (SiMe<sub>3</sub>) ppm. Trace (5%) amounts of Fp-SiMe<sub>3</sub>, 7.57 ppm, and Fp-SiMe<sub>2</sub>SiMe<sub>3</sub>, -3.62 and 3.33 ppm, also were observed. Continued irradiation for 2 h led to formation of Fp-SiMe<sub>3</sub> as the ultimate iron-containing product, recovered in 66% yield.

## Reactivity of Coordinated [Ph<sub>2</sub>PCHP(S)Ph<sub>2</sub>]<sup>-</sup> and [Ph<sub>2</sub>P(S)CHP(S)Ph<sub>2</sub>]: Two-Center, Regiospecific Reactivity in Rhodium and Iridium Complexes and Formation of a Disubstituted Methylene Bridge between Platinum Atoms

Jane Browning, Keith R. Dixon,\* and Robert W. Hills

Department of Chemistry, University of Victoria  
Victoria, British Columbia, Canada, V8W 2Y2

Received August 31, 1988

**Summary:** Reaction of methyl iodide with [Ir{Ph<sub>2</sub>P(S)CHP(S)Ph<sub>2</sub>}(cod)] occurs in a regiospecific sequence to form first [Ir{Ph<sub>2</sub>P(S)CHMeP(S)Ph<sub>2</sub>}(cod)]I and only subsequently [IrMeI{Ph<sub>2</sub>P(S)CHMeP(S)Ph<sub>2</sub>}(cod)]I. For [Rh{Ph<sub>2</sub>PCHP(S)Ph<sub>2</sub>}(cod)] the addition sequence is reversed. [Pt{Ph<sub>2</sub>P(S)CHP(S)Ph<sub>2</sub>}(MeOcod)] shows both ligand and metal site reactivity in transforming to a novel dimer, [Pt<sub>2</sub>{Ph<sub>2</sub>P(S)CP(S)Ph<sub>2</sub>}(MeOcod)<sub>2</sub>], containing a quaternary carbon bridge between two platinum centers. The bridging carbon is part of four-member C,S chelate rings at both platinum.

The coordination chemistry of bis(diphenylphosphino)methane (dppCH<sub>2</sub>) is extensive and well-known.<sup>1</sup> Although the majority of studies have been concerned with reactivity at metal centers in dinuclear complexes bridged by dppCH<sub>2</sub>,<sup>1</sup> reactivity at the methylene carbon has also attracted interest. Thus reactions of M(CO)<sub>4</sub>(dppCH<sub>2</sub>) (M = Cr, Mo, or W) and MCl<sub>2</sub>(dppCH<sub>2</sub>) (M = Pd or Pt) with bases followed by alkyl halides can result in either mono- or dialkylation at the methylene carbon.<sup>2</sup> Several complexes are known involving metalation at the methylene carbon of a coordinated dppCH<sub>2</sub>,<sup>3</sup> including two examples of double metalation, [(AcOHg)<sub>2</sub>C(PPh<sub>2</sub>HgOAc)<sub>2</sub>]<sup>3a</sup> and [(PhNC)<sub>4</sub>Fe{(Ph<sub>2</sub>P)<sub>2</sub>C(AuPPh<sub>3</sub>)<sub>2</sub>}]<sup>3c</sup> and a particularly unusual example involving carbene-like coordination in the polymer, [Pt(μ-Cl)<sub>2</sub>Pd=C(PPh<sub>2</sub>)<sub>2</sub>]<sub>n</sub>.<sup>4</sup>

Corresponding work on Ph<sub>2</sub>PCH<sub>2</sub>P(S)Ph<sub>2</sub> (dpp(S)CH<sub>2</sub>) and Ph<sub>2</sub>P(S)CH<sub>2</sub>P(S)Ph<sub>2</sub> (dpp(S)<sub>2</sub>CH<sub>2</sub>) has been much less extensive.<sup>5</sup> Coordination via (P,S) for dpp(S)CH<sub>2</sub> and dpp(S)CH<sup>-</sup> via (S) or (S,S) for dpp(S)<sub>2</sub>CH<sub>2</sub>,<sup>8-10</sup> and via (S,S) or (S,C) for dpp(S)<sub>2</sub>CH<sup>-</sup>,<sup>10-12</sup> have all been reported but the ability of the sulfides to delocalize charge and enhance the acidity (reactivity) of the methylene protons relative to dppCH<sub>2</sub> has been little studied. We now report

(1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99-127.

(2) Al-Jibori, S.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 286-287; *Inorg. Chim. Acta* **1982**, *65*, L123-124.

(3) (a) Lusser, M.; Peringer, P. *Organometallics* **1984**, *3*, 1916-1917 and references therein. (b) Uson, R.; Laguna, A.; Laguna, M.; Gimeno, M. A.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986**, 509-510. (c) Riera, V.; Ruiz, J. *J. Organomet. Chem.* **1986**, *310*, C36-C38.

(4) Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 1710-1711.

(5) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982-1987 and references therein.

(6) Berry, D. E.; Browning, J.; Dixon, K. R.; Hills, R. W. *Can. J. Chem.* **1988**, *66*, 1272-1282.

(7) Lusser, M.; Peringer, P. *Inorg. Chim. Acta* **1987**, *127*, 151-152.

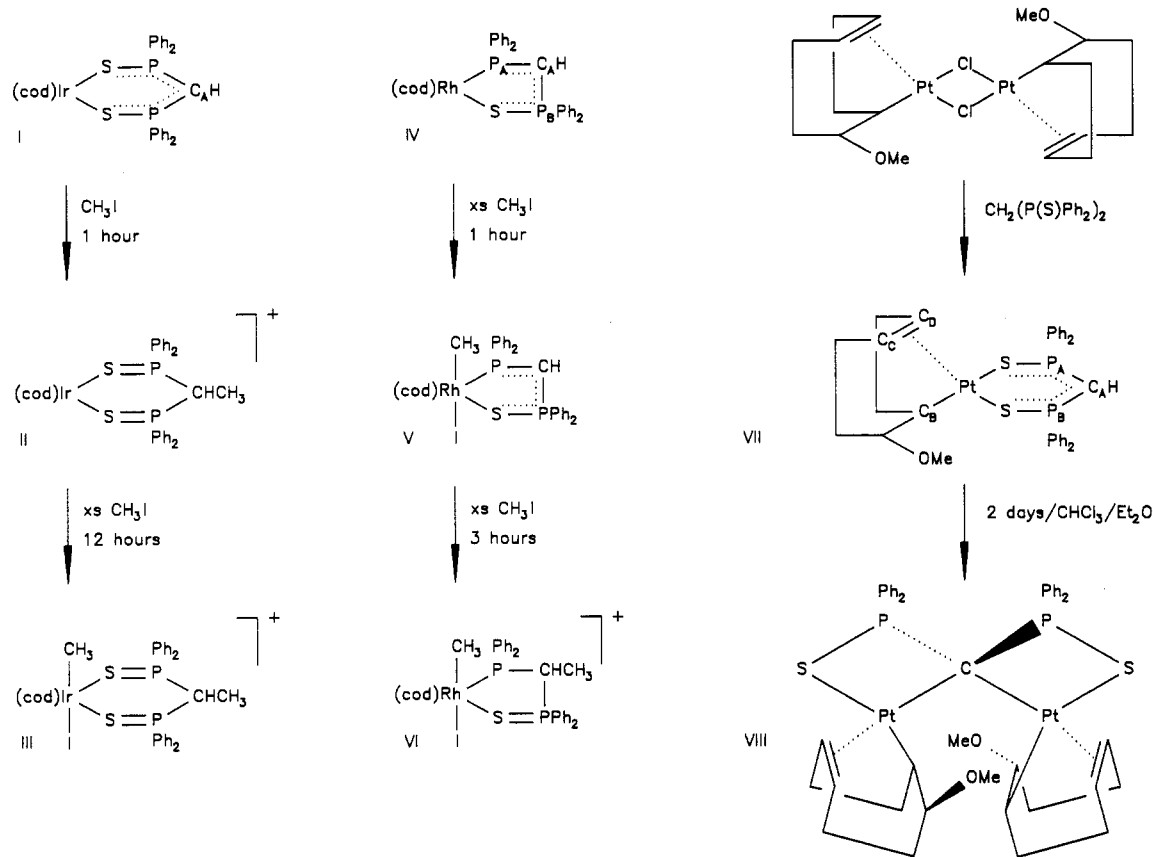
(8) Ainscough, E. W.; Brodie, A. M.; Furness, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2360-2363.

(9) Ainscough, E. W.; Brodie, A. M.; Mentzer, E. *J. Chem. Soc., Dalton Trans.* **1973**, 2167-2171.

(10) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 2226-2228.

(11) Davison, A.; Reger, D. L. *Inorg. Chem.* **1971**, *10*, 1967-1970.

(12) Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986**, *315*, 269-276.

Scheme I. Reactions of  $[\text{Ph}_2\text{PCHP}(\text{S})\text{Ph}_2]^-$  and  $[\text{Ph}_2\text{P}(\text{S})\text{CHP}(\text{S})\text{Ph}_2]^-$  Complexes

two unusual aspects of this chemistry, both involving the combination of metal- and ligand-centered (possibly metal-mediated) reactivity. First, in rhodium and iridium complexes where the metal is susceptible to oxidative addition, we illustrate the previously unexplored possibility of sequential, two-center reactivity where one site is on the ligand and the other on the metal; and second, we describe double metalation of  $\text{dpp}(\text{S}_2)\text{CH}_2$  to form a novel, dinuclear platinum complex containing a disubstituted methylene bridge with C,S chelation at both platinum centers.

The cations  $[\text{M}(\text{dpp}(\text{S}_n)\text{CH}_2)(\text{cod})]^+$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ;  $\text{cod} = \text{cycloocta-1,5-diene}$ ;  $\text{dpp}(\text{S}_n)\text{CH}_2 = \text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$ <sup>13</sup> or  $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ )<sup>9</sup> are readily prepared by reactions of  $[\text{M}(\mu\text{-Cl})(\text{cod})]_2$ , with  $\text{dpp}(\text{S}_n)\text{CH}_2$  in acetone with  $\text{NaBF}_4$ .<sup>14</sup> Deprotonation of the cations by sodium hydride in tetrahydrofuran yields  $[\text{M}(\text{dpp}(\text{S}_n)\text{CH})(\text{cod})]$  (e.g. I and IV in Scheme I).<sup>15</sup> As in the related platinum and palladium complexes,<sup>6</sup> the state of substitution at the central

carbon of the  $\text{dpp}(\text{S}_n)\text{CH}_n$  ligand can be probed by using <sup>31</sup>P and <sup>13</sup>C NMR,<sup>16</sup> and the reactions shown in Scheme I are easily monitored. When  $[\text{Ir}\{\text{dpp}(\text{S}_2)\text{CH}\}(\text{cod})]$  (I) reacts with 1 molar equiv of methyl iodide, the initial attack is at the methine site of the ligand to form II rather than the expected oxidative addition product. The carbon of the added methyl group in II appears at 13.59 ppm in the <sup>13</sup>C spectrum, very close to the 12.57 ppm of  $[\text{Ph}_2\text{P}(\text{S})\text{CHMeP}(\text{S})\text{Ph}_2]$ . Moreover, relative to the starting material I, the  $\text{C}_A$  resonance of II is deshielded and <sup>1</sup>J-( $\text{C}_A\text{-P}$ ) sharply reduced (I, 15.41 ppm and 95 Hz; II, 31.34 ppm and 39 Hz), as expected for attack at the ligand site.<sup>6</sup> By contrast, subsequent oxidative addition from II to III is very slow (20% conversion over 12 h,  $\delta(\text{CH}_3\text{Ir})$  11.62 ppm), and decomposition begins before pure product can be isolated.<sup>17</sup> This contrasts with  $[\text{Rh}\{\text{dpp}(\text{S})\text{CH}\}(\text{cod})]$  (IV), which reacts first at the metal center and only subsequently at the ligand site. NMR evidence shows that formation of V proceeds to completion before the ligand-centered reaction begins, but we were unable to isolate V without contamination by the ultimate product VI.<sup>17,18</sup>

Addition of 2 molar equiv of  $\text{dpp}(\text{S}_2)\text{CH}_2$  to  $[\text{Pt}(\mu\text{-Cl})(\text{MeOcod})]_2$  ( $\text{MeOcod} = 8\text{-methoxy-cyclooct-4-ene-1-yl}$ ) in acetone with  $\text{NaBF}_4$  yields a colorless, crystalline solid,  $[\text{Pt}(\text{dpp}(\text{S}_2)\text{CH})(\text{MeOcod})]$  (VII), in which a methylene proton of the phosphorus ligand has been removed. In

(13) <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 62.9 (reference SiMe<sub>4</sub>) and 101.3 (reference 85% H<sub>3</sub>PO<sub>4</sub>) MHz. Satisfactory microanalyses were obtained for all new complexes except III and V which were not isolated. Anal. Calcd for  $[\text{Rh}\{\text{dpp}(\text{S})\text{CH}_2\}(\text{cod})]\text{BF}_4$  (Found): C, 55.5 (56.2); H, 4.80 (4.22);  $[\text{Ir}\{\text{dpp}(\text{S})\text{CH}_2\}(\text{cod})]\text{BF}_4$ : C, 49.3 (48.7); H, 4.26 (4.26). Calcd for I (Found): C, 53.0 (53.8); H, 4.45 (4.68). Calcd for  $[\text{II}]^+\text{I}^-\text{CH}_2\text{Cl}_2$  (Found): C, 43.1 (43.8); H, 3.93 (4.00). Calcd for IV (Found): C, 63.3 (63.2); H, 5.31 (5.35). Calcd for VI (Found): C, 46.2 (46.2); H, 4.32 (4.57). Calcd for VII (Found): C, 52.2 (52.3); H, 4.64 (5.10). Calcd for  $[\text{Pt}(\text{C}_8\text{H}_{15})\{\text{dpp}(\text{S})\text{CCH}_3\}]\cdot 0.5\text{CH}_2\text{Cl}_2$  (Found): C, 50.9 (51.0); H, 4.69 (4.72). Calcd for VIII (Found): C, 46.3 (45.9); H, 4.52 (4.71).

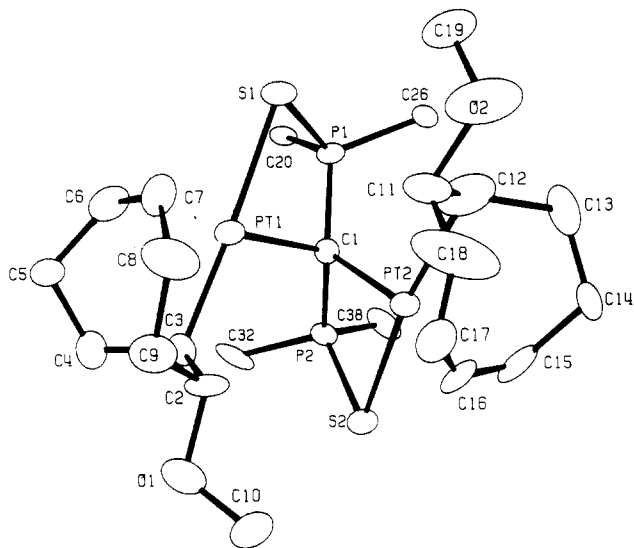
(14)  $[\text{M}\{\text{Ph}_2\text{P}_A\text{C}_A\text{H}_2\text{P}_B(\text{S})\text{Ph}_2\}(\text{cod})]^+$ ,  $\text{M} = \text{Rh}$  (Ir):  $\delta(\text{C}_A)$  38.5 (37.7) ppm, <sup>1</sup>J( $\text{C}_A\text{-P}_A$ ) = 18 (25) Hz, <sup>1</sup>J( $\text{C}_A\text{-P}_B$ ) = 55 (56) Hz;  $\delta(\text{P}_A)$  40.2 (30.1) ppm, <sup>1</sup>J( $\text{Rh-P}_A$ ) = 148 Hz,  $\delta(\text{P}_B)$  57.9 (62.3) ppm, <sup>2</sup>J( $\text{P-P}$ ) = 51 (45) Hz.  $[\text{M}\{\text{Ph}_2\text{P}(\text{S})\text{C}_A\text{H}_2\text{P}(\text{S})\text{Ph}_2\}(\text{cod})]^+$ ,  $\text{M} = \text{Rh}$  (Ir):  $\delta(\text{C}_A)$  32.9 (32.3) ppm, <sup>1</sup>J( $\text{C}_A\text{-P}$ ) = 48 (46) Hz;  $\delta(\text{P})$  36.8 (32.6) ppm, <sup>2</sup>J( $\text{Rh-P}$ ) = 4.9 Hz.

(15)  $[\text{M}\{\text{Ph}_2\text{P}_A\text{C}_A\text{HP}_B(\text{S})\text{Ph}_2\}(\text{cod})]$ ,  $\text{M} = \text{Rh}$  (Ir):  $\delta(\text{C}_A)$  26.3 (26.1) ppm, <sup>1</sup>J( $\text{C}_A\text{-P}_A$ ) = 59 (68) Hz, <sup>1</sup>J( $\text{C}_A\text{-P}_B$ ) = 119 (122) Hz;  $\delta(\text{P}_A)$  41.6 (36.7) ppm, <sup>1</sup>J( $\text{Rh-P}_A$ ) = 137 Hz,  $\delta(\text{P}_B)$  54.2 (59.4) ppm, <sup>2</sup>J( $\text{P-P}$ ) = 121 (112) Hz.  $[\text{M}\{\text{Ph}_2\text{P}(\text{S})\text{C}_A\text{HP}(\text{S})\text{Ph}_2\}(\text{cod})]$ ,  $\text{M} = \text{Rh}$  (Ir):  $\delta(\text{C}_A)$  13.4 (15.4) ppm, <sup>1</sup>J( $\text{C}_A\text{-P}$ ) = 91 (95) Hz;  $\delta(\text{P})$  36.0 (34.1) ppm, <sup>2</sup>J( $\text{P-Rh}$ ) = 4.5 Hz.

(16) Typically, deprotonation results in sharp increases in <sup>2</sup>J( $\text{P-P}$ ) and <sup>1</sup>J( $\text{C}_A\text{-P}(\text{S})$ ) and increased shielding of  $\text{C}_A$ .

(17) NMR suggests that the added methyl and iodide groups in III and V are mutually trans, but this is not completely certain.

(18) V:  $\delta(\text{CH}_3\text{Rh})$  13.5 ppm, <sup>1</sup>J( $\text{C-Rh}$ ) = 9.5 Hz.  $\delta(\text{P}_A)$  47.8 ppm,  $\delta(\text{P}_B)$  54.1 ppm, <sup>1</sup>J( $\text{Rh-P}_A$ ) = 139 Hz, <sup>2</sup>J( $\text{Rh-P}_B$ ) < 5 Hz, <sup>2</sup>J( $\text{P-P}$ ) = 153 Hz. VI:  $\delta(\text{P}_A)$  48.4 ppm,  $\delta(\text{P}_B)$  56.9 ppm, <sup>1</sup>J( $\text{Rh-P}_A$ ) = 138 Hz, <sup>2</sup>J( $\text{Rh-P}_B$ ) < 5 Hz, <sup>2</sup>J( $\text{P-P}$ ) = 58 Hz. The "clean" NMR spectra of VI suggest a single pair of enantiomers, possibly those with C-CH<sub>3</sub> syn to Rh-CH<sub>3</sub>, the stereochemistry expected if addition to the ligand occurred via the metal.



**Figure 1.** Molecular structure of VIII,  $[\text{Pt}_2\{\text{Ph}_2\text{P}(\text{S})\text{CP}(\text{S})\text{-Ph}_2\}(\text{MeOcod})_2]$ . For clarity, only one carbon is shown for each of the four phenyl rings.

toluene- $d_6$  solution  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR evidence<sup>19</sup> indicates an S,S-bonded structure, but in more polar solvents, such as  $\text{CDCl}_3$  or tetrahydrofuran- $d_6$ , rapid exchange of the two phosphorus environments occurs at ambient temperatures and slow exchange limit  $^{31}\text{P}$  spectra are not obtained until  $-70^\circ\text{C}$ . Line-shape analysis gives  $\Delta G^\ddagger$  as 49  $\text{kJ mol}^{-1}$  in tetrahydrofuran. Interestingly, the corresponding methyl-substituted complex  $[\text{Pt}\{\text{Ph}_2\text{P}(\text{S})\text{CMeP}(\text{S})\text{Ph}_2\}(\text{MeOcod})]^{20}$  shows no dynamic exchange at ambient temperatures, and the  $^{31}\text{P}$  spectrum in dimethyl- $d_6$  sulfoxide does not coalesce until  $60^\circ\text{C}$  ( $\Delta G^\ddagger = 66 \text{ kJ mol}^{-1}$ ). If exchange occurs by dissociation of one end of the bound ligand followed by reorganization of the three-coordinate platinum intermediate before recoordination of the ligand, then a determining factor in these rates could be solvation of the "dangling"  $\text{P}=\text{S}$  group in the intermediate. It is not clear, however, why the presence of a methyl group should have such a large influence on this process.

The subsequent reactivity of VII is a combination of ligand- and metal-centered processes with gradual formation of a novel dimer, VIII, in which  $[\text{C}\{\text{P}(\text{S})\text{Ph}_2\}_2]^{2-}$  forms a quaternary carbon bridge between two platinum centers.<sup>21</sup> The bridging carbon is part of four-member, C,S chelate rings at both platinum. An X-ray diffraction study (Figure 1)<sup>22</sup> shows the two approximately square-planar platinum centers inclined at  $90.1^\circ$  to each other and a very distorted tetrahedron around carbon with  $\text{P}-\text{C}-\text{P} = 127.2^\circ$  and the other angles ca.  $94^\circ$ . The complex is

(19) VII:  $\delta(\text{C}_A)$  15.6 ppm,  $^1J(\text{C}_A-\text{P}) = 96 \text{ Hz}$ ,  $^2J(\text{C}_A-\text{Pt}) = 96 \text{ Hz}$ ,  $\delta(\text{C}_B)$  33.2 ppm,  $^1J(\text{C}_B-\text{Pt}) = 638 \text{ Hz}$ ,  $\delta(\text{C}_{C/D})$  85.5/88.4 ppm,  $^1J(\text{C}_{C/D}-\text{Pt}) = 184/181 \text{ Hz}$ ;  $\delta(\text{P}_A)$  33.8 ppm,  $^2J(\text{Pt}-\text{P}_A) = \text{ca. } 50 \text{ Hz}$ ,  $\delta(\text{P}_B)$  38.1 ppm,  $^2J(\text{Pt}-\text{P}_B) = 125 \text{ Hz}$ ,  $J(\text{P}-\text{P}) = 11 \text{ Hz}$ .

(20)  $\delta(\text{C}_A)$  14.6 ppm,  $^1J(\text{C}_A-\text{P}) = 108 \text{ Hz}$ ,  $^2J(\text{C}_A-\text{Pt}) = 64 \text{ Hz}$ ,  $\delta(\text{C}_B)$  33.7 ppm,  $^1J(\text{C}_B-\text{Pt}) = 625 \text{ Hz}$ ,  $\delta(\text{C}_{C/D})$  84.6/87.9 ppm,  $^1J(\text{C}_{C/D}-\text{Pt}) = 188/186 \text{ Hz}$ ;  $\delta(\text{P}_A)$  33.5 ppm,  $^2J(\text{Pt}-\text{P}_A) = 42 \text{ Hz}$ ,  $\delta(\text{P}_B)$  38.6 ppm,  $^2J(\text{Pt}-\text{P}_B) = 107 \text{ Hz}$ ,  $J(\text{P}-\text{P}) = 51 \text{ Hz}$ .

(21) VIII:  $\delta(\text{P})$  48.33 ppm,  $J(\text{P}-\text{Pt}) = 337$  and  $12.2 \text{ Hz}$ ,  $J(\text{P}-\text{P}) = 23.9 \text{ Hz}$ .

(22) Crystal data at  $25^\circ\text{C}$ : monoclinic, space group  $\text{C}2/c$  (No. 15);  $a = 19.033(4)$ ,  $b = 14.145(4)$ ,  $c = 29.794(4) \text{ \AA}$ ;  $\beta = 99.49(2)^\circ$ ;  $V(\text{cell}) = 7911.23 \text{ \AA}^3$ ;  $D_{\text{measd}} = 1.83 \text{ g cm}^{-3}$  (floatation in  $\text{CCl}_4/\text{CHBr}_3$ ),  $D_{\text{calcd}} = 1.87 \text{ g cm}^{-3}$ ; formula  $\text{C}_{43}\text{H}_{50}\text{O}_2\text{P}_2\text{Pt}_2\text{S}_2$ ;  $M_r = 1115.12$ ;  $Z = 8$ . Asymmetric unit = one molecule. Intensity measurements were collected for two reciprocal space octants ( $h$  unrestricted,  $k \geq 0$ ,  $l \geq 0$ ) up to  $2\theta = 50^\circ$  on a CAD-4 diffractometer and corrected for Lorentz, polarization, and absorption effects. Refinement was by full-matrix least-squares calculations of 455 variable parameters based on 2188 independent reflections to give  $R = 0.040$  and  $R_w = 0.040$  at the present stage of refinement. Details are given in the supplementary material.

remarkable both as the first example of a complexed  $[\text{C}\{\text{P}(\text{S})\text{Ph}_2\}_2]^{2-}$  ion and as a disubstituted methylene-bridged species. Methylene bridges which are unsupported by metal-metal bonds are relatively rare,<sup>23</sup> as are methylene bridges of any type between platinum atoms.<sup>23,24</sup> The concept of linking metal centers with a strongly bound bridge accompanied by relatively labile<sup>10,25</sup> pendant arms may lead to unusual chemistry both at the metals and at the bridge.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for a research grant.

**Supplementary Material Available:** Tables of fractional atomic coordinates, anisotropic temperature parameters, interatomic distances, bond angles, and selected intermolecular distances (8 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.

(23) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojilovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400-1406.

(24) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159-263.

(25) Browning, J.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1986**, *25*, 1987-1992.

### Diastereoselective Synthesis of Chiral Clusters from the Reaction of Chiral (Propargyl alcohol) $\text{Co}_2(\text{CO})_8$ with Triphenylphosphine

David H. Bradley, Masood A. Khan,<sup>†</sup> and Kenneth M. Nicholas\*

Department of Chemistry, University of Oklahoma  
Norman, Oklahoma 73019

Received September 6, 1988

**Summary:** Dicobalt hexacarbonyl complexes of chiral (racemic) propargylic alcohols **1** react with  $\text{PPh}_3$  to form the diastereomeric complexes  $[\text{R}^1\text{C}\equiv\text{CCH}(\text{OH})\text{R}^2]_{\text{Co}_2}(\text{CO})_5\text{PPh}_3$  (**2**) with diastereomeric excesses (% de) ranging from 10 to  $>95\%$ . The isomeric complexes can be separated chromatographically and exhibit significant configurational stability, isomerizing only over a period of days at room temperature. The relative stereochemistry of the major isomer **2b** ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Ph}$ ) has been established by X-ray diffraction.

The lure of cluster-promoted asymmetric reactions and catalysis has stimulated interest in the preparation and properties of chiral cluster complexes.<sup>1</sup> However, prospects for achieving this goal have dimmed somewhat with the appearance of recent reports of several chiral tetranuclear  $\text{MM}'_2\text{C}_2$  and  $\text{M}_2\text{M}'_2\text{C}$  and pentanuclear  $\text{M}_2\text{M}'_2\text{C}_2$  clusters which racemize on the NMR time scale.<sup>1-4</sup> An exception has been found recently in the case of some diastereomeric ( $\mu$ -acyl)trisodium clusters<sup>5</sup> which equili-

<sup>†</sup> Address correspondence regarding the X-ray diffraction results to this author.

(1) Reviews: McGlinchey, M. J.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Marinetti, A.; Saillard, J.-Y.; Jaouen, G. *Can. J. Chem.* **1983**, *61*, 1319. Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

(2) Jaouen, G.; Marinetti, A.; Saillard, J.-Y.; Sayer, B. C.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 225.

(3) Sutin, K. A.; Kolis, J. W.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A.; Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1987**, *6*, 439.

(4) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123.

(5) Halvenston, M. C.; Lynch, T. J. *Organometallics* **1987**, *6*, 208.