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## Hard Ligands as Donors to Soft Metals. 4. Cationic Bis(solvent) Complexes of Palladium(II) and Platinum(II) Containing Monodentate Tertiary Phosphine Ligands

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A series of palladium(II) and platinum(II) complexes  $[M(PR_3)_2(solvent)_2](Y)_2$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2, PPh_3$ ; solvent = py, dmsO,  $Me_2CO$ ;  $Y = ClO_4, PF_6$ ) have been isolated and characterized. The dmsO ligands are all oxygen-bonded. Acetone is a very weak ligand readily displaced by moisture, olefins, and even perchlorate ions. The catalytic activity of the acetone complexes in the isomerization and hydrogenation of oct-1-ene is described and compared with that of the chloride-bridged dimeric complexes  $[M_2(\mu-Cl)_2(PR_3)_4](ClO_4)_2$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2$ ) in acetone solution.

### Introduction

Palladium(II) and platinum(II) complexes containing weakly bonded ligands have been widely implicated in catalytic cycles. However, only a few such complexes have been isolated and characterized so that relatively little is known about the factors that influence their stability. In previous studies<sup>1-5</sup> palladium(II) and platinum(II) complexes of weakly bonded ligands stabilized by the bidentate tertiary phosphine ligand dppe<sup>6</sup> have been described. In the present work the monodentate phosphines  $PPh_3$  and  $PMePh_2$  were used to allow the complexes an unconstrained choice of geometry.  $PPh_3$  was chosen because it is the most widely used tertiary phosphine in organometallic and coordination chemistry.  $PMePh_2$  simulates closely the electronic properties of dppe and is therefore particularly suitable for studying the effects of freely chosen coordination geometry as compared to an imposed cis coordination. The appearance of the methyl signal in the <sup>1</sup>H NMR spectrum is, of course, particularly valuable for determining the geometry.<sup>7</sup>

The donor ligands studied were pyridine, dimethyl sulfoxide, and acetone. Pyridine is a relatively strong donor ligand that can be classified as a borderline base in the context of Pearson's HSAB approach.<sup>4,8</sup> It provides a suitable model for studying weaker ligands. Dimethyl sulfoxide is particularly interesting because it contains two potential donor sites. It forms very stable complexes with the platinum metals when coordinating through sulfur. Bonding through the oxygen atom, on the other hand, is of intermediate strength and usually observed only in cases where steric constraints dominate. Finally, acetone is a very modest donor ligand so that although many acetone complexes have been inferred to exist, relatively few have actually been isolated.<sup>3-5</sup> All previously isolated ketone complexes of palladium(II) and platinum(II) have involved  $\eta^1$ -coordination via oxygen.  $\eta^2$ -Coordination via the C=O bond has only been observed for zerovalent metal complexes of ketones containing strongly electron-withdrawing substituents, e.g.  $[M(PPh_3)_2(CF_2X)_2CO]$  ( $M = Pd, Pt$ ;  $X = F, Cl^9$ ).

The present paper accordingly reports the preparation, isolation, and characterization of a series of solvent complexes  $[M(PR_3)_2(solvent)_2](Y)_2$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2, PPh_3$ ; solvent = py, dmsO,  $Me_2CO$ ;  $Y = ClO_4, PF_6$ ).

In previous work we found the acetone complex  $[Pd(dppe)(Me_2CO)_2](ClO_4)_2$  to be an effective catalyst for the hydrogenation of oct-1-ene and styrene under ambient conditions.<sup>3,10</sup> It

was of interest therefore to examine the catalytic ability of the present acetone complexes in the isomerization and hydrogenation of olefins. The ability of the chloride-bridged platinum(II) complex  $[PtCl(\mu-Cl)(2,4,6-Me_3py)]_2$  to promote the homogeneous catalysis of olefin hydrogenation was attributed to the ease with which the chloride-bridge is cleaved to yield the monomeric solvent complex.<sup>11</sup> In the light of this and the evidence presented below that the chloride-bridged complexes  $[M_2(\mu-Cl)_2(PR_3)_4](ClO_4)_2$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2$ ) yield monomeric acetone complexes in acetone solution, the ability of these chloride-bridged tertiary phosphine complexes to catalyze olefin isomerization and hydrogenation was also examined.

### Experimental Section

*cis*- $[MCl_2(PR_3)_2]$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2$ ;  $M = Pt, PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2, PPh_3$ ), *trans*- $[PdCl_2(PPh_3)_2]$ , and  $[M_2(\mu-Cl)_2(PR_3)_4](ClO_4)_2$  ( $M = Pd, Pt$ ;  $PR_3 = 1/2 Ph_2PCH_2CH_2PPh_2, PMePh_2$ ) were prepared as described previously<sup>1,2,12</sup> and characterized spectroscopically and microanalytically. Solvents were redistilled and stored as described previously.<sup>1,2</sup> Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer, <sup>1</sup>H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 40.3 MHz on a Jeol FX100 spectrometer relative to an external 85% phosphoric acid standard. Elemental analyses were performed by Elemental Microanalysis Ltd. and Butterworth Laboratories Ltd. Satisfactory analyses were obtained for all the complexes except  $[Pt(PPh_3)_2(dmsO)_2]X_2$  ( $X = ClO_4, PF_6$ ) and the bis(acetone) complexes.

**Syntheses.** All manipulations of solvent complexes were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk apparatus. Light was excluded from all reactions involving silver(I) salts. **Caution!** Perchlorate salts are potentially explosive and should only be prepared in small quantities; no such problems were encountered in any of the syntheses reported, but *great care* must always be exercised.

**Pyridine Complexes.** *cis*- $[M(PMePh_2)_2(py)_2](ClO_4)_2$  ( $M = Pd, Pt$ ) and *cis*- $[Pt(PPh_3)_2(py)_2](ClO_4)_2$  were prepared by adding a solution of silver perchlorate (2 mmol) in nitromethane (20 mL) to a well-stirred solution of  $[MCl_2(PR_3)_2]$  (1 mmol) ( $M = Pd, Pt$ ;  $PR_3 = PMePh_2$ ) in dichloromethane (20 mL) containing pyridine (10 mL). When  $M = Pt$  and  $PR_3 = PPh_3$ , nitromethane (20 mL) and pyridine (5 mmol) were added to a dichloromethane (20 mL) solution of the complex. Silver chloride precipitated rapidly, although the solutions were stirred for 3 h at room temperature to ensure completeness of reaction. After filtration and concentration in vacuo, dropwise addition of diethyl ether precipitated a white solid, which was recrystallized from nitromethane/diethyl ether; yield 50%.

$[Pd(PPh_3)_2(py)_2](ClO_4)_2$  was prepared as described above except that pyridine (3 mmol) was not added initially, but was added only after the silver chloride precipitate had been removed. After the solution was stirred for 30 min, the white crystalline product was obtained in the same way as before in 54% yield.

**Dimethyl Sulfoxide Complexes.** *cis*- $[Pd(PR_3)_2(dmsO)_2](PF_6)_2$  ( $PR_3 = PMePh_2, PPh_3$ ) were prepared by adding a solution of silver hexafluorophosphate (2 mmol) in nitromethane (30 mL) to a well-stirred suspension of  $[PdCl_2(PR_3)_2]$  (1 mmol) in dichloromethane (20 mL) containing dimethyl sulfoxide (3 mmol). Silver chloride precipitated immediately although the solutions were stirred for 3 h at room temperature to ensure completeness of reaction. After filtration and evaporation of the solvent in vacuo, the residue was dissolved in nitromethane

- (1) Part 1: Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* 1979, 1705.
- (2) Part 2: Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* 1980, 19, 2299.
- (3) Part 3: Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* 1980, 2246.
- (4) Davies, J. A.; Hartley, F. R. *Chem. Rev.* 1981, 81, 79.
- (5) Hartley, F. R.; Davies, J. A. *Rev. Inorg. Chem.* 1982, 4, 27.
- (6) dppe =  $Ph_2PCH_2CH_2PPh_2$ .
- (7) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* 1966, 770.
- (8) Jensen, W. B. *Chem. Rev.* 1978, 78, 1.
- (9) Clarke, B.; Green, M.; Osborn, R. B. L.; Stone, F. G. A. *J. Chem. Soc. A* 1968, 167.
- (10) Davies, J. A.; Hartley, F. R.; Murray, S. G.; Marshall, G. *J. Mol. Catal.* 1981, 10, 171.

(11) Rumin, R. *J. Organomet. Chem.* 1983, 247, 351.

(12) Hartley, F. R. *Organomet. Chem. Rev.* 1970, A6, 119.

**Table I.** Analytical and Infrared Spectroscopic Data for Bis(pyridine) Complexes

complex	color	% C <sup>a</sup>	% H <sup>a</sup>	% N <sup>a</sup>	8a(py)/cm <sup>-1</sup> <sup>b</sup>	9a(py)/cm <sup>-1</sup> <sup>b</sup>	$\nu(\text{ClO}_4^-)$ /cm <sup>-1</sup>
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	49.5 (50.05)	4.2 (4.2)	3.25 (3.25)	1608 m	1210 m	1090 s, 620 s
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	45.3 (45.4)	3.8 (3.8)	2.95 (2.95)	1610 s	1215 m	1090 s, 620 s
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	56.0 (55.9)	4.1 (4.1)	2.8 (2.8)	1608 s	1211 m	1085 s, 620 s
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	50.85 (51.3)	3.8 (3.75)	2.6 (2.6)	1610 m	1215 m	1095 s, 620 s

<sup>a</sup> Found (calcd). <sup>b</sup> For pyridine IR band notation, see: Gill, N. S.; Nuttall, R. H.; Scaife, D. R.; Sharp, D. W. A. *J. Inorg. Nucl. Chem.* **1961**, *18*, 79 and references therein.

**Table II.** <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR<sup>a</sup> Spectroscopic Data for Bis(solvent) Complexes (Solvent = py, dmsO)

complex	$\delta(\text{aromatic})/\text{ppm}$	$\delta(\text{py H}_\alpha)/\text{ppm}$	$\delta(\text{PMePh}_2)/\text{ppm}$	$\delta(\text{Me}_2\text{SO})/\text{ppm}$	$\delta(^{31}\text{P})/\text{ppm}^b$
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.10–7.85 m (6.9)	8.65 d (1.0) <sup>c</sup>	2.13 d (1.6) <sup>d</sup>		13.2 s
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.10–7.90 m (6.7)	8.65 m (1.0) <sup>e</sup>	2.16 m (1.6) <sup>f</sup>		-11.9 s <sup>g</sup>
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.00–8.00 m (9.1)	8.65 d (1.0) <sup>h</sup>			20.7 s
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (py) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.00–8.00 m (9.1)	8.66 m (1.0) <sup>i</sup>			3.1 s <sup>j</sup>
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (dmsO) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	7.35–7.82 m (3.5)		2.08 d (1.0) <sup>k</sup>	2.52 s (2.1)	24.2 s
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (dmsO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.35–7.90 m (3.4)		2.12 m (1.0) <sup>l</sup>	2.62 s (2.1)	m
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (dmsO) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	7.30–8.00 m (2.6)			2.45 s (1.0)	37.7 s

<sup>a</sup> In CD<sub>3</sub>NO<sub>2</sub> solutions at room temperature. <sup>b</sup> Relative to external 85% H<sub>3</sub>PO<sub>4</sub>; positive value indicates a shift to higher frequency. <sup>c</sup> <sup>3</sup>J<sub>H-H</sub> = 4 Hz. <sup>d</sup> |<sup>2</sup>J<sub>P-H</sub> + <sup>4</sup>J<sub>P-H</sub>| = 9 Hz. <sup>e</sup> <sup>3</sup>J<sub>P-H</sub> = 28 Hz. <sup>f</sup> <sup>3</sup>J<sub>H-H</sub> = 5 Hz. <sup>g</sup> <sup>3</sup>J<sub>P-H</sub> = 40 Hz. <sup>h</sup> |<sup>2</sup>J<sub>P-H</sub> + <sup>4</sup>J<sub>P-H</sub>| = 10 Hz. <sup>i</sup> <sup>1</sup>J<sub>P-P</sub> = 3160 Hz. <sup>j</sup> <sup>3</sup>J<sub>H-H</sub> = 4 Hz. <sup>k</sup> <sup>1</sup>J<sub>P-H</sub> = 26 Hz. <sup>l</sup> <sup>3</sup>J<sub>H-H</sub> = 5 Hz. <sup>m</sup> <sup>1</sup>J<sub>P-P</sub> = 3276 Hz. <sup>n</sup> |<sup>2</sup>J<sub>P-H</sub> + <sup>4</sup>J<sub>P-H</sub>| = 10 Hz. <sup>o</sup> <sup>1</sup>J<sub>P-H</sub> = 44 Hz. <sup>p</sup> |<sup>2</sup>J<sub>P-H</sub> + <sup>4</sup>J<sub>P-H</sub>| = 11 Hz. <sup>q</sup> See text.

and the solution filtered. The solid was precipitated by dropwise addition of diethyl ether. Recrystallization from nitromethane/diethyl ether gave a yellow solid in 59% yield (PMePh<sub>2</sub>) and 49% yield (PPh<sub>3</sub>).

[Pt(PMePh<sub>2</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared in 65% yield by essentially the same method as just described, using silver perchlorate (2 mmol) in nitromethane (20 mL) and 10 mmol of dimethyl sulfoxide.

It proved impossible to prepare pure samples of either the perchlorate or hexafluorophosphate salts of [Pt(PPh<sub>3</sub>)<sub>2</sub>(dmsO)<sub>2</sub>]<sup>2+</sup> by the methods just described. A 10% yield of a crude sample of the hexafluorophosphate and a 55% yield of a crude sample of the perchlorate were obtained, but in both cases it proved extremely difficult to isolate the white solid product, which was unstable, darkening with age.

**Acetone Complexes.** *cis*-[M(PR<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (PR<sub>3</sub> = <sup>1</sup>/<sub>2</sub> Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPH<sub>2</sub> (M = Pd, Pt), PMePh<sub>2</sub> (M = Pd, Pt), PPh<sub>3</sub> (M = Pd)) were prepared by adding a solution of silver perchlorate (2 mmol) in dry acetone (25 mL) to [MCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (1 mmol) dissolved or suspended in dichloromethane (25 mL). Rapid precipitation of silver chloride occurred, although the reaction mixture was stirred for 3 h to ensure completeness of reaction before the solid was filtered off, the filtrate was concentrated in vacuo to 20 mL, and diethyl ether (50 mL) was added very carefully so as to form two layers, which when mixed together very slowly over 1–2 h induced precipitation of a fine solid in 50–70% yield. The products were characterized by infrared and <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, being insufficiently stable to allow microanalyses to be performed.

[Pd(OCIO<sub>3</sub>)(dppe)(Me<sub>2</sub>CO)](ClO<sub>4</sub>) was prepared by treating [PdCl<sub>2</sub>(dppe)] (1 mmol) with silver perchlorate (2 mmol) in dry benzene (25 mL) containing dry acetone (25 mL). After rapid precipitation of silver chloride, the solution was stirred for a further 3 h to ensure completeness of reaction. Cautious evaporation led to precipitation of a fine white solid in 50% yield. The product was shown to be [Pd(OCIO<sub>3</sub>)(dppe)(Me<sub>2</sub>CO)](ClO<sub>4</sub>) by infrared and <sup>1</sup>H NMR spectroscopy but was insufficiently stable to undergo microanalysis.

**Catalyses.** The acetone complexes (0.2 mmol) were prepared in situ in a mixture of dichloromethane (25 mL) and acetone (25 mL). After the silver chloride was filtered off, oct-1-ene (4 mmol) was added and the mixtures were stored under nitrogen in a thermostatically controlled bath at 25 °C for 6 days. An identical procedure but with replacement of the nitrogen atmosphere by hydrogen was used for the hydrogenations under 1 atm of hydrogen. Experiments at higher hydrogen pressures were performed in a 500-mL stainless steel autoclave (Baskerville and Lindsay Ltd., Manchester, England), which was cleaned regularly by heating a solution of triphenylphosphine in toluene to 80 °C under 15 atm of hydrogen for several hours. Blank runs were performed at intervals with oct-1-ene under hydrogen in the same 1:1 dichloromethane/acetone solvent system but in the absence of catalyst to confirm that the reaction vessel remained catalytically inert.

Product analyses for octane, oct-1-ene, *cis*- and *trans*-oct-2-ene, *trans*-oct-3-ene, and *trans*-oct-4-ene were initially performed on a Pye 204 gas-liquid chromatograph equipped with a flame ionization detector and a 50 m × 0.3 mm glass capillary column coated with OV17 as the stationary phase at 25 °C and using nitrogen as the carrier gas. Peak areas, which were determined by a planimeter, were found to be proportional to concentration. Later analyses were performed at 30 °C on a Perkin-Elmer Sigma 3B gas-liquid chromatograph interfaced with a

Perkin-Elmer Sigma 15 data station and fitted with a Chromopack CPSIL5 CB 25 m × 0.32 mm column using helium carrier gas.

## Results and Discussion

**Pyridine Complexes.** In previous work most of the characterized bis(solvent) complexes of palladium(II) and platinum(II) have been prepared by total halide abstraction from the corresponding dichloro complex using a silver salt in the presence of the solvent.<sup>3,13</sup> However, while this reaction was effective for the platinum(II) complexes and for palladium(II) with PMePh<sub>2</sub>, the analogous reaction with [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was less straightforward. It led to the desired [Pd(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> contaminated with a silver pyridine complex, either [Ag(py)<sub>4</sub>](ClO<sub>4</sub>)<sup>14</sup> or AgCl·py.<sup>15</sup> Accordingly, [Pd(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared from the dichloro complex by precipitation of silver chloride in dichloromethane. After filtration, addition of pyridine to what was presumably a solution of [Pd(OCIO<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (see below) followed by diethyl ether led to the formation of a white solid characterized as *cis*-[Pd(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. It is quite possible that small amounts of silver(I)-pyridine adducts were formed during the preparation of the other bis(pyridine) complexes but removed during the several recrystallizations necessary to obtain analytically pure samples. It is probably significant that [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] is considerably less soluble than the other starting complexes with the result that reaction with silver perchlorate takes place more slowly in this case, allowing more time for reaction of silver(I) with pyridine.

Infrared and <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the bis(pyridine) complexes indicated that all the complexes were of *cis* geometry (Tables I and II).

**Dimethyl Sulfoxide Complexes.** The palladium(II)-dimethyl sulfoxide complexes [Pd(PR<sub>3</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (PR<sub>3</sub> = PMePh<sub>2</sub>, PPh<sub>3</sub>) were obtained by chloride abstraction from [PdCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] using silver hexafluorophosphate. Infrared and <sup>1</sup>H NMR data (Tables II and III) were all consistent with *cis* complexes containing oxygen-bonded dmsO ligands.<sup>16</sup> Oxygen coordination here, as previously observed in [Pd(dppe)(dmsO)<sub>2</sub>]<sup>+</sup>Y<sup>-</sup> (Y = ClO<sub>4</sub>, PF<sub>6</sub>), is believed to be a consequence of the high steric demands of the phosphine ligands; PPh<sub>3</sub>, PMePh<sub>2</sub>, and dppe have effective cone angles of 145, 136, and 125°, respectively.<sup>17</sup>

Neither of the two platinum(II)-bis(dimethyl sulfoxide) complexes was obtained as a single pure species. [Pt(PMePh<sub>2</sub>)<sub>2</sub>-

(13) Hartley, F. R.; Murray, S. G.; Porter, C. J. Unpublished results.

(14) Nilsson, K.; Oskarsson, A. *Acta Chem. Scand.* **1982**, *A36*, 605.

(15) Healy, P. C.; Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 111 and references therein.

(16) Cotton, F. A.; Francis, R.; Horrocks, W. D. *J. Phys. Chem.* **1960**, *64*, 1534.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

**Table III.** Analytical and Infrared Spectroscopic Data for Bis(dimethyl sulfoxide) Complexes

complex	color	% C <sup>a</sup>	% H <sup>a</sup>	$\nu(\text{S}=\text{O})/\text{cm}^{-1}$	$\rho_r(\text{CH}_3)/\text{cm}^{-1}$	$\nu([\text{X}]^-)/\text{cm}^{-1}$
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (dms <sub>2</sub> )](PF <sub>6</sub> ) <sub>2</sub>	yellow	38.05 (37.8)	4.2 (4.0)	960 m, 940 m	980 m	835 s, 558 s
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (dms <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	white	38.1 (37.9)	4.1 (4.05)	920 s	977 m	1090 s, 620 s
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (dms <sub>2</sub> )](PF <sub>6</sub> ) <sub>2</sub>	yellow	44.7 (44.6)	4.1 (3.95)	960 m, 940 m	990 s	840 s, 558 s
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (dms <sub>2</sub> )](PF <sub>6</sub> ) <sub>2</sub>	white	40.0 (41.2)	3.65 (3.65)	912 s	990 m	835 s, 558 s
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (dms <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	white	41.7 (44.7)	3.6 (3.9)	908 s	982 s	1085 s, 620 s

<sup>a</sup> Found (calcd).**Table IV.** Infrared and <sup>1</sup>H<sup>a</sup> and <sup>31</sup>P{<sup>1</sup>H}<sup>b</sup> NMR Spectroscopic Data for Bis(acetone) Complexes

complex	color	$\nu(\text{C}=\text{O})/\text{cm}^{-1}$	$\nu(\text{ClO}_4^-)/\text{cm}^{-1}$	$\delta(\text{aromatic})/\text{ppm}$	$\delta(\text{PCH}_2\text{CH}_2\text{P})$ or $\delta(\text{PMePh}_2)/\text{ppm}$	$\delta(\text{Me}_2\text{CO})/\text{ppm}$	$\delta(^{31}\text{P})/\text{ppm}^c$
[Pd(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	1647 s	1090 s, 620 s	7.50–8.50 m (4.9)	3.07 m (1.0) <sup>d</sup>	2.15 s (3.0)	73.8 s
[Pt(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	1625 s	1095 s, 620 s	7.40–8.60 m (5.0)	2.87 m (1.0) <sup>e</sup>	2.18 s (2.9)	36.8 s <sup>f</sup>
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	yellow	1650 s	1085 s, 620 s	7.40–7.90 m (3.3)	2.19 m (1.0) <sup>g</sup>	2.14 s (2.0)	24.7 s
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	white	1625 s	1085 s, 620 s	7.10–8.30 m (3.4)	2.16 m (1.0) <sup>h</sup>	2.20 s (2.1)	-9.0 s <sup>i</sup>
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	yellow	1650 s, 1630 s	1090 s, 622 s	7.20–8.30 m (2.6)		2.16 s (1.0)	j
[Pd(OCIO <sub>3</sub> )(dppe)(Me <sub>2</sub> CO)](ClO <sub>4</sub> )	pale yellow	1668 s	1090 s, 620 s	7.50–8.50 m (5.0)	3.08 m (1.0) <sup>k</sup>	2.15 s (1.6)	j

<sup>a</sup> In CD<sub>3</sub>NO<sub>2</sub> at room temperature. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (1:1 v/v) at room temperature. <sup>c</sup> Relative to external 85% H<sub>3</sub>PO<sub>4</sub>; positive value indicates a shift to higher frequency. <sup>d</sup> <sup>2</sup>J<sub>P-H</sub> + <sup>3</sup>J<sub>P-H</sub> = 24 Hz. <sup>e</sup> <sup>2</sup>J<sub>P-H</sub> + <sup>3</sup>J<sub>P-H</sub> = 19 Hz. <sup>f</sup> <sup>1</sup>J<sub>Pt-P</sub> = 3932 Hz. <sup>g</sup> <sup>2</sup>J<sub>P-H</sub> = 12 Hz, <sup>4</sup>J<sub>P-H</sub> = 2 Hz; <sup>2</sup>J<sub>P-H</sub> and <sup>4</sup>J<sub>P-H</sub> have opposite signs. <sup>h</sup> <sup>3</sup>J<sub>Pt-H</sub> = 46 Hz, <sup>2</sup>J<sub>P-H</sub> + <sup>4</sup>J<sub>P-H</sub> = 11 Hz. <sup>i</sup> <sup>1</sup>J<sub>Pt-P</sub> = 3931 Hz. <sup>j</sup> <sup>31</sup>P{<sup>1</sup>H} NMR spectrum not recorded. <sup>k</sup> <sup>2</sup>J<sub>P-H</sub> + <sup>3</sup>J<sub>P-H</sub> = 24 Hz.

(dms<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> was obtained in a microanalytically pure form with infrared (bands at 977 and 920 cm<sup>-1</sup>) and <sup>1</sup>H NMR (dms<sub>2</sub> methyls: singlet at 2.52 ppm) spectra both indicating oxygen bonding.<sup>1,16</sup> The phosphine methyl <sup>1</sup>H NMR signal was a doublet with corresponding <sup>195</sup>Pt satellites indicative of a cis configuration. However, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contained numerous signals with <sup>195</sup>Pt satellites, suggesting the presence of several phosphorus-containing platinum species in solution. Heating the sample to +70 °C led to little change in the relative signal intensities. It is tentatively suggested that the complexity of the spectrum indicates the presence of cis and trans isomers. Sulfur coordination of the dms<sub>2</sub> ligands is considered unlikely because the <sup>1</sup>H NMR spectrum clearly indicates only oxygen coordination<sup>4</sup> and examination of space-filling molecular models strongly suggests that steric hindrance would prevent coordination via sulfur even if the two phosphine ligands lay trans to one another.

Attempts to isolate [Pt(PPh<sub>3</sub>)<sub>2</sub>(dms<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> and its perchlorate analogue were unsuccessful. Both compounds were difficult to recrystallize, and the elemental analyses obtained (Table III) were less than satisfactory.

**Acetone Complexes.** Previous work clearly indicated that it would be very difficult to isolate acetone complexes. They are extremely sensitive to moisture, with water readily displacing acetone.<sup>3,4</sup> Attempts to prepare [Pd(PR<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PPh<sub>3</sub>) by chloride abstraction using silver hexafluorophosphate in acetone produced solutions that, according to conductivity measurements, contained 2:1 electrolytes but solutions from which bis(acetone) complexes could not be isolated.<sup>18</sup> Attempts to repeat the earlier preparation<sup>19</sup> of [Pd(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> led not to the expected bis(acetone) complex, but rather to the mono(acetone) complex [Pd(OCIO<sub>3</sub>)(dppe)(Me<sub>2</sub>CO)](ClO<sub>4</sub>). This showed infrared absorptions at 1668 cm<sup>-1</sup> due to coordinated acetone,<sup>20</sup> at 1090 and 620 cm<sup>-1</sup> due to uncoordinated perchlorate,<sup>21a</sup> and at 1140, 1010, and 875 cm<sup>-1</sup> due to coordinated perchlorate.<sup>3,21b,22–25</sup> Integration of the <sup>1</sup>H NMR signals showed an acetone:dppe ratio of 1:1. Accordingly, it was concluded that when the reaction product was precipitated from benzene solution containing very little acetone, the perchlorate

ion successfully competed with the weak  $\sigma$ -donor acetone for coordination to palladium(II).

Accordingly, in the present work the acetone complexes were always prepared and isolated in the presence of excess acetone. In this way [Pd(PR<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (PR<sub>3</sub> = <sup>1</sup>/<sub>2</sub> Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, PPh<sub>3</sub>, PMePh<sub>2</sub>) were prepared. None showed infrared bands at 1140, 1010, or 875 cm<sup>-1</sup>, indicative of coordinated perchlorate. The dppe complex showed strong absorptions at 1647 cm<sup>-1</sup>, due to coordinated acetone,<sup>20</sup> and at 1085 and 622 cm<sup>-1</sup>, due to uncoordinated perchlorate, and integration of the <sup>1</sup>H NMR spectrum confirmed an acetone:dppe ratio of 2:1. In the absence of excess acetone throughout, mixed acetone-perchlorate complexes were obtained with both PMePh<sub>2</sub> and PPh<sub>3</sub>. However, using excess acetone allowed *cis*-[Pd(PPh<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> to be obtained. It exhibited infrared absorptions at 1650 and 1630 cm<sup>-1</sup>, indicative of cis coordination of two acetone ligands,<sup>20,26</sup> as well as at 1090 and 620 cm<sup>-1</sup>, due to uncoordinated perchlorate. The <sup>1</sup>H NMR spectrum showed an acetone:PPh<sub>3</sub> ratio of 1:1. *cis*-[Pd(PMePh<sub>2</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was very similar (Table IV).

The initial procedure used to isolate [Pt(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> involved evaporation of the solvent in vacuo and trituration of the resultant oil with diethyl ether or *n*-hexane. The resultant product contained the desired bis(acetone) complex together with a significant quantity of a second compound, as indicated by an anomalous band in the infrared spectrum at 1030 cm<sup>-1</sup> and additional peaks in the methyl region of the <sup>1</sup>H NMR spectrum. Comparison of the infrared and <sup>1</sup>H NMR spectra with those of the complex formed by reaction of 2 equiv of silver perchlorate with [PtCl<sub>2</sub>(dppe)] in the presence of 4-hydroxy-4-methylpentan-2-one indicated that the second complex formed alongside the bis(acetone) complex arose from reaction with 4-hydroxy-4-methylpentan-2-one. Although this ligand may be formed by interaction of acetone with platinum(II), it is most likely to be formed during the drying of acetone, as shown previously.<sup>19</sup> On evaporation of the acetone in vacuo, relatively high concentrations of 4-hydroxy-4-methylpentan-2-one, which boils at 164–166 °C under 11 mm of mercury pressure,<sup>27</sup> would be formed, enabling it to compete against acetone for coordination to platinum(II). Accordingly, [Pt(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was isolated as a single pure complex by precipitation in the presence of excess acetone.

[Pt(PMePh<sub>2</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, isolated in the presence of excess acetone, was shown to be of cis geometry by the phosphine methyl <sup>1</sup>H NMR signals, which consisted of a doublet with corresponding <sup>195</sup>Pt satellites. Both this and the dppe complex

(18) Roberts, N. K.; Skelton, B. W.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1982**, 2093.

(19) Davies, J. A. Ph.D. Thesis, London University (external at the Royal Military College of Science), 1980.

(20) Driessen, W. L.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 977.(21) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley Interscience: New York, 1986: (a) p 138; (b) pp 251–3.(22) Hester, R. E.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 769.(23) Pavkovic, S. F.; Meek, D. W. *Inorg. Chem.* **1965**, *4*, 1091.(24) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331.(25) Uson, R.; Fornies, J.; Martinez, F. J. *Organomet. Chem.* **1976**, *112*, 105.(26) Dehand, J.; Pfeffer, M.; Zinsius, M. *J. Organomet. Chem.* **1976**, *118*, C62.(27) *Handbook of Chemistry and Physics*, 67th ed.; Chemical Rubber Co.: Boca Raton, FL, 1986.

**Table V.** Catalytic Isomerization of Oct-1-ene in the Absence of Hydrogen<sup>a</sup>

catalyst precursor	reactn time/days	% compn of octene mixture				
		1	cis-2	trans-2	trans-3	trans-4
[Pd(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	84.4	4.9	3.0	7.0	0.7
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	0.4	15.9	48.5	33.2	2.0
[Pt(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	49.9	16.2	16.2	15.1	2.6
	4 <sup>b</sup>	2.9	15.8	36.4	39.3	5.6
[Pt(PMePh <sub>2</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	62.6	14.4	13.1	8.6	1.3
[Pd <sub>2</sub> (μ-Cl) <sub>2</sub> (dppe) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	96.6	0.6	0.7	2.1	0.0
[Pd <sub>2</sub> (μ-Cl) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	95.7	0.5	2.2	1.6	0.0
	4 <sup>b</sup>	47.1	12.8	35.6	3.9	0.5
[Pt <sub>2</sub> (μ-Cl) <sub>2</sub> (dppe) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	80.3	7.2	3.0	7.8	1.7
[Pt <sub>2</sub> (μ-Cl) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	95.9	0.05	0.5	1.6	1.95

<sup>a</sup> T = 25 °C; [oct-1-ene] = 8 × 10<sup>-2</sup> M; [metal complex] = 4 × 10<sup>-3</sup> M; in CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (1:1 v/v). <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub> only.

show large <sup>1</sup>J<sub>Pt-P</sub> coupling constants of 3931 and 3932 Hz, respectively, indicating coordination of the phosphine ligands trans to a ligand of weak trans influence.<sup>28</sup>

It is interesting to note that while the geometry of the dppe complexes is necessarily cis, the complexes with the monodentate phosphines are also cis, despite the fact that this is the more sterically demanding configuration. This is consistent with previous observations of antisymbiotic behavior in soft metal complexes containing hard oxygen donor ligands such as [Ir(H)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, where the acetone ligands are mutually cis and are trans to the hydride ligands,<sup>29</sup> and a number of palladium(II) complexes containing bidentate C-N ligands in which acetone binds trans to the softer aromatic carbon atom rather than opposite the harder nitrogen donor.<sup>26,30</sup>

Many workers do not isolate their acetone complexes, but rather prepare them in situ, as indeed was done in the catalytic work reported later in this paper. It is essential that the silver perchlorate used in such preparations be stored in a dry inert atmosphere in the dark. Failure to observe these precautions results in degradation of the silver(I) salt and leads to incomplete chloride abstraction and subsequent contamination of the desired product by the dimeric chloride-bridged species [M<sub>2</sub>(μ-Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>. In order to ensure that this did not occur in the present work, authentic samples of the chloride-bridged dimers (M = Pd, Pt; PR<sub>3</sub> = 1/2 Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, PMePh<sub>2</sub>) were prepared and their spectra used in comparison with those of authentic bis(acetone) complexes. The spectra were all as expected except for that of [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, which in dichloromethane/acetone (1:1 v/v) solution showed in its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum a phosphorus resonance at 47.3 ppm (<sup>1</sup>J<sub>Pt-P</sub> = 3787 Hz), together with two signals of approximately equal intensity at 44.9 ppm (<sup>1</sup>J<sub>Pt-P</sub> = 3513 Hz) and 34.4 ppm (<sup>1</sup>J<sub>Pt-P</sub> = 4016 Hz). In dichloromethane alone only the 47.3 ppm signal is observed. It thus appears that, when dissolved in dichloromethane/acetone, the dimeric species is in equilibrium with a small amount of monomeric [PtCl(dppe)(Me<sub>2</sub>CO)](ClO<sub>4</sub>); the phosphorus signal at 34.4 ppm, which has the larger coupling constant, is assumed to represent the phosphine trans to the weaker acetone ligand. The observation of only a single phosphorus signal in dichloromethane/acetone solutions of [M<sub>2</sub>(μ-Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Pd, PR<sub>3</sub> = 1/2 Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, PMePh<sub>2</sub>; M = Pt, PR<sub>3</sub> = PMePh<sub>2</sub>) suggests that insignificant bridge splitting occurs with these complexes.

During the course of this work several pertinent points arose concerning the preparation, isolation, and use of acetone complexes:

1. As previously noted,<sup>3,4</sup> acetone complexes are extremely sensitive to moisture.
2. Acetone is a very weak donor ligand for palladium(II) and platinum(II) and is thus easily displaced by other ligands such

as perchlorate ligands; accordingly, all isolations should be effected in the presence of acetone.

3. Because acetone is such a weak donor ligand, it is essential to ensure that no chloride ligands remain, or chloride dimer formation will occur; accordingly, very pure silver(I) salts should always be used.

4. In the present work perchlorate ligands were used. Although no untoward incidents were observed, this should not be taken for granted.<sup>4,19</sup> All perchlorate complexes should be treated *with great care* and all preparations carried out on the smallest scale possible.

**Oct-1-ene Isomerization in the Absence of Hydrogen.** When a 20-fold excess of oct-1-ene was treated with [M(PR<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [M<sub>2</sub>(μ-Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Pd, Pt; PR<sub>3</sub> = 1/2 Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, PMePh<sub>2</sub>) in 1:1 acetone/dichloromethane solution at 25 °C for several days under nitrogen, only limited olefin isomerization took place (Table V). Examination of the solutions by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed that the initial complexes were still the only phosphorus-containing species present at the end of the reaction. Olefins are known to form only very weak complexes with palladium(II) and platinum(II) cations in the sense that olefins are readily displaced by other stronger ligands.<sup>31</sup> It therefore is interesting to note that isomerization is greater in the absence of added acetone. We believe that this is due to the lack of competition between acetone and oct-1-ene for coordination to the metal center. It is significant that, of the chloride-bridged dimeric complexes, [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, which showed the greatest tendency to form the monomeric acetone complex in solution (see above), is the most active complex in promoting oct-1-ene isomerization. A reviewer has, however, suggested that the enhanced isomerization rate in the absence of acetone may well arise from the reduced dielectric constant of the medium, which facilitates the energetics of reaching the transition state.

**Oct-1-ene Hydrogenation and Isomerization in the Presence of Hydrogen.** [M(PR<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [M<sub>2</sub>(μ-Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Pd, Pt; PR<sub>3</sub> = 1/2 Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, PMePh<sub>2</sub>) all actively promoted the isomerization of oct-1-ene in 1:1 acetone/dichloromethane solution at 25 °C under hydrogen (Tables VI and VII). Thus, the mechanism for olefin isomerization in the presence of hydrogen must be different from that in its absence.

The observation that the monodentate tertiary phosphine complexes [M(PMePh<sub>2</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>]<sup>2+</sup> are more effective isomerization catalysts than their dppe analogues is consistent with a theoretical model of ethene insertion into the Pt-H bond of [PtH(PH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup>, which indicates that the most energetically favorable reaction pathway is one in which the P-Pt-P angle opens from an initial 95° in the starting cis complex to 110° in the transition state.<sup>32</sup> Clearly, while this is possible in the PMePh<sub>2</sub> complexes, it is not possible in the dppe complexes.

It is apparent (Table VI) that the rate of isomerization of oct-1-ene catalyzed by [Pt(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Pd<sub>2</sub>-

(28) Pregosin, P. S.; Kunz, R. W. *<sup>31</sup>P and <sup>13</sup>C NMR Spectroscopy of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin and Heidelberg, 1979; p 42.

(29) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. P.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354.

(30) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

(31) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

(32) Thorn, D. L.; Hoffmann, R. J. *Am. Chem. Soc.* **1978**, *100*, 2079.

**Table VI.** Catalytic Hydrogenation and Isomerization of Oct-1-ene in the Presence of  $[M(PR_3)_2(Me_2CO)_2](ClO_4)_2^a$ 

catalyst precursor	P(H <sub>2</sub> )/atm	reactn time/h	% compn of octene/octane mixture						appearance of soln	metal ppt?	
			octane	1	cis-2	trans-2	trans-3	trans-4			
[Pd(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1	3	0.0	2.0	12.3	31.4	38.5	15.8	unchanged	no	
		23	0.0	0.8	8.4	32.0	38.2	20.6	sl darker	yes	
	15	0.03	1	3	23	24.5	39.5	9	unchanged	?	
		20	10	1	10	31.5	34.5	13	sl darker	yes	
		30	1	3	0.5	8.5	34.5	39	15	sl darker	?
		26	40.5	0	6	20.5	23	10	dark yellow	yes	
[Pd(PMePh <sub>2</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1	3	0.0	1.0	8.0	31.9	37.4	21.7	unchanged	no	
		23	0.0	1.0	10.8	30.6	37.0	20.6	red/brown	yes	
	15	0.03	2	86	4	8	<i>b</i>	<i>b</i>	unchanged	?	
		22	48	2.5	5	17	19	8.5	red/brown	yes	
		30	2	9.5	1	8.5	30.5	36.5	14	orange	?
		24	42	0.5	6	19	23.5	9	red/brown	yes	
[Pt(dppe)(Me <sub>2</sub> CO) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1	3	0.0	55.8	17.4	6.1	17.9	2.8	unchanged	no	
		23	7.2	0.9	9.7	30.1	33.6	18.5	pale green	yes	
	1 <sup>c</sup>	3.2	9.3	2.4	30.1	18.2	35.5	4.5	pale green	no	
		1 <sup>d</sup>	3.2	7.8	2.6	28.3	18.4	37.9	5.0	pale green	no
		15	0.17	2.5	81	4	6.5	6	<i>b</i>	unchanged	no
		0.75	44.5	4.5	12.5	12	21.5	5	pale green	?	
	30	1.33	66	0	3	12	13	5.5	pale green	?	
		2	70	0	2.5	11	11	5.5	pale green	?	
		3.75	81	0	0	7	8	4	pale green	yes	
		2	91	0	0	4	4	1	pale green	?	
		3	91	0	0	3.5	4	1.5	pale green	yes	
		1	3	0.0	0.4	25.6	37.5	27.7	8.8	unchanged	no
15		21	2.7	1.4	8.5	30.4	38.6	18.4	pale yellow	yes	
23.5		40	1.5	6	22	22.5	8	yellow/brown	yes		
30	0.25	3.5	74	6.5	10	6	<i>b</i>	pale yellow	?		
	1	21.5	22.5	17	20.5	15.5	3	yellow	?		
	3	36	2.5	17	23	18.5	3	yellow	?		
	19	45.5	1	8	24.5	17	4	yellow/brown	yes		

<sup>a</sup>  $T = 25$  °C; [oct-1-ene] =  $8 \times 10^{-2}$  M; [metal complex] =  $4 \times 10^{-3}$  M; in CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (1:1 v/v). <sup>b</sup> Obscured by larger peak. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub> only. <sup>d</sup> In CH<sub>2</sub>Cl<sub>2</sub> only, in the presence of Hg(0).

**Table VII.** Catalytic Hydrogenation and Isomerization of Oct-1-ene in the Presence of  $[M_2(\mu-Cl)_2(PR_3)_4](ClO_4)_2^a$ 

catalyst precursor	P(H <sub>2</sub> )/atm	reactn time/h	% compn of octene/octane mixture						appearance of soln	metal ppt?
			octane	1	cis-2	trans-2	trans-3	trans-4		
[Pd <sub>2</sub> (μ-Cl) <sub>2</sub> (dppe) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1	3	0.0	48.0	18.8	7.7	20.9	4.6	unchanged	no
		23	0.0	0.0	27.4	17.5	46.2	8.9	unchanged	no
	15	3	0	25.5	26	13.5	28	7	unchanged	?
		28	5	2	8.5	32	38.5	14	sl darker	yes
		30	2	1	16.5	29	39.5	12	unchanged	?
		27	8	1	8.5	13.5	36	15	yellow/brown	yes
[Pd <sub>2</sub> (μ-Cl) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1	3	0.0	96.0	0.7	1.6	1.7	0.0	unchanged	no
		22	1.6	46.4	12.5	30.6	7.4	1.5	light orange	no
	1 <sup>b</sup>	3.5	0.0	68.5	8.0	20.8	2.2	0.5	unchanged	no
		15	3	2	23	30	17	5	unchanged	no
		19.5	77	0	0	7	11	6	deep red <sup>c</sup>	no
		46	98	0	0	0	1	1	deep red <sup>c</sup>	no
30	4	1	12	21.5	45.5	16	4	unchanged	no	
	22	28	1	7.5	29	26	8.5	red <sup>c</sup>	no	
	48	77	0	0	4.5	10	4.5	red <sup>c</sup>	no	
	1	3	1.7	85.7	5.7	1.6	4.6	0.7	unchanged	no
[Pt <sub>2</sub> (μ-Cl) <sub>2</sub> (dppe) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	15	23	3.0	21.1	31.1	10.1	29.9	4.8	unchanged	no
		1.5	5.5	71	7	8	9	<i>d</i>	unchanged	no
	30	24	33.5	5	18	14	24	5.5	pale green	yes
		3	3	84	3	7	3	<i>d</i>	unchanged	no
		20	23.5	56	6	7.5	7	<i>d</i>	pale green	yes
		1	3	1.8	43.1	15.3	23.1	14.2	2.5	unchanged
15	23	2.9	1.0	10.5	34.9	32.3	18.4	unchanged	no	
	3	5	77	6	7	5	<i>d</i>	unchanged	no	
	21	15	6	17	40	17	5	yellow/green	yes	
	30	2	15	40	12	20	10	3	unchanged	no
30	24	33	1.5	6.5	33	20.5	5.5	yellow	yes	

<sup>a</sup>  $T = 25$  °C; [oct-1-ene] =  $8 \times 10^{-2}$  M; [metal complex] =  $2 \times 10^{-3}$  M; in CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (1:1 v/v). <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub> only. <sup>c</sup> See text for details. <sup>d</sup> Obscured by larger peak.

(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> under 1 atm of hydrogen was approximately doubled when the 1:1 acetone/dichloromethane solvent was replaced by dichloromethane alone. This is presumably a consequence of the elimination of competition between oct-1-ene and excess acetone for coordination to the platinum(II). It also

indicates that the presence of solvent ligands is not essential for chloride-bridge cleavage; presumably the olefin can also effect it.

Under 1 atm of hydrogen no visible decomposition was apparent during the isomerization reaction although, once isomerization

was complete, decomposition to form pale green (platinum(II)) or deep red (palladium(II)) solutions indicated the formation of colloidal metal. The observation of this decomposition raised the question as to whether it was colloidal metal or the metal complex that was the active catalyst. An attempt to resolve this by vigorously stirring a solution with metallic mercury to suppress the catalytic activity of the metallic platinum present<sup>33</sup> certainly had no influence on the rate of reaction, strongly suggesting that it was the metal complexes that were the active species.

Although hydrogenation was not apparent under 1 atm of hydrogen, it did take place at higher pressures. In the case of the palladium(II) bis(acetone) complexes, very rapid oct-1-ene isomerization took place at higher hydrogen pressures, followed by slow hydrogenation accompanied by extensive decomposition and precipitation of metallic palladium. In the case of the platinum(II) bis(acetone) complexes, the rate of hydrogenation at higher hydrogen pressures was enhanced so as to be comparable to the isomerization rate. In contrast to the case with isomerization reported above, the dppe platinum complex was more effective than its PMePh<sub>2</sub> analogue in promoting hydrogenation, although there was no significant difference between the palladium complexes. As in the case of the palladium system, decomposition to metallic platinum was observed.

The behavior of [Pd<sub>2</sub>(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> at higher hydrogen pressures was noteworthy. For the first period of the reaction the solutions remained yellow and appeared unchanged. However, after about 20 h a deep red color was observed, while GC analysis showed the formation of significant quantities of octane. The deep red solutions were insensitive to light and could

be stored under a nitrogen atmosphere for several days without change. On exposure to air, the deep red solution returned to its original yellow color and no metallic palladium was precipitated. In the absence of oct-1-ene, a solution of [Pd<sub>2</sub>(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> in 1:1 dichloromethane/acetone became slightly orange when exposed to 15 atm of hydrogen for 48 h at 25 °C. On the readmittance of air for a short period, the original yellow coloration was restored, and a small amount of metallic palladium was precipitated. These observations tend to suggest that the unidentified red species is stabilized by oct-1-ene. This red species is strongly reminiscent of the remarkable red palladium(I) complex [Pd<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> observed during the alcoholysis of silanes catalyzed by [Pd(dppe)(ROH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.<sup>10</sup>

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**Registry No.** [Pd(PMePh<sub>2</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-80-7; [Pt(PMePh<sub>2</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-82-9; [Pd(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-84-1; [Pt(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118245-51-5; [Pd(PMePh<sub>2</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 118206-86-3; [Pt(PMePh<sub>2</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-88-5; [Pd(PPh<sub>3</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 118206-90-9; [Pt(PPh<sub>3</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 118206-92-1; [Pt(PPh<sub>3</sub>)<sub>2</sub>(dmsO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-93-2; [Pd(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 75845-46-4; [Pt(dppe)(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-95-4; [Pd(PMePh<sub>2</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-97-6; [Pt(PMePh<sub>2</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118206-99-8; [Pd(PPh<sub>3</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118226-08-7; [Pd(OClO<sub>2</sub>)(dppe)(Me<sub>2</sub>CO)](ClO<sub>4</sub>)<sub>2</sub>, 118207-01-5; [Pd<sub>2</sub>(μ-Cl)<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 72476-84-7; [Pd<sub>2</sub>(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118207-03-7; [Pd<sub>2</sub>(μ-Cl)<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 73558-22-2; [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(dppe)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 118226-09-8; *cis*-[PdCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)], 19978-61-1; *cis*-[PdCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>], 29484-75-1; *cis*-[PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)], 14647-25-7; *cis*-[PtCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>], 16633-72-0; *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], 15604-36-1; *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], 28966-81-6; oct-1-ene, 111-66-0.

(33) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* 1985, 4, 1819 and references therein.

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## Selective Oxidations of Olefins Catalyzed by Platinum(II) Complexes. Use of *tert*-Butyl Hydroperoxide and Potassium Caroate as Oxidants: Ketone vs Epoxide Formation

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Four low-cost oxidants have been tested in the oxidation of olefins catalyzed by either [(diphoe)Pt(CF<sub>3</sub>)(CH<sub>2</sub>Cl<sub>2</sub>)]BF<sub>4</sub> or (diphoe)Pt(CF<sub>3</sub>)(OH) (diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene) under mild conditions. These include sodium hypochlorite, sodium perborate, *tert*-butyl hydroperoxide, and potassium hydroperoxysulfate (caroate). While the first two are inactive, with the second two, selective ketonization of the olefin or selective epoxidation (including terminal olefins) can be obtained. A discussion is also included concerning the origin of selectivity in this class of catalysts based essentially on steric factors.

### Introduction

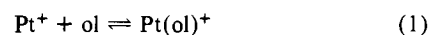
Interest in the selective epoxidation of olefins with transition-metal complexes is still high since epoxides are very important building blocks in the petrochemical industry.<sup>2</sup>

We have recently reported<sup>3,4</sup> on a platinum(II) system that is able to catalyze very efficiently the selective epoxidation of simple terminal olefins with diluted (5–35%) hydrogen peroxide. Typical catalysts are complexes of the type P<sub>2</sub>Pt(CF<sub>3</sub>)X (P<sub>2</sub> = diphosphine; X = solvent, –OH) that play a bifunctional role in the system (Scheme I) since (i) they activate otherwise unreactive olefins toward nucleophilic attack and (ii) they increase H<sub>2</sub>O<sub>2</sub> nucleophilicity by forming Pt–OOH species through acid–base reactions.

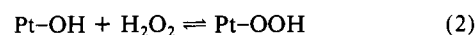
This system is highly chemoselective since epoxides are the only detectable oxidation products. Moreover, by modifying the catalysts with chiral diphosphines it has been possible to obtain also enantioselective epoxidation of simple olefins<sup>5</sup> with optical purities up to 41% in the case of propylene oxide.

### Scheme I

olefin activation



increase H<sub>2</sub>O<sub>2</sub> nucleophilicity



ol = olefin

(1) (a) University of Venice. (b) University of Padua.  
(2) Sheldon, R. A. *Aspects Homogeneous Catal.* 1981, 4, 3.  
(3) Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* 1984, 1538.  
(4) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* 1985, 107, 7563.

(5) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* 1987, 6, 728.