Some Novel Reactions of Tri-*tert*-butylphosphine with Iridium(III), Rhodium(III), Platinum(II), and Palladium(II) Chlorides

Ram G. Goel* and William O. Ogini

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received December 7, 1981

Treatment of excess of tri-*tert*-butylphosphine with hydrated iridium(III) or rhodium(III) chloride, in DMF, at room temperature, affords intractable products which seem to contain iridium(III) or rhodium(III) hydrido complexes and protonated phosphine. Reaction in refluxing DMF gave *trans*-$MCl(CO)[P\text{-}t\text{-}Bu)_2H]_2$, **1** (M = Ir) and **2** (M = Rh), in quantitative yields. Treatment of $P(t\text{-}Bu)_3$ with $PtCl_2$ or K_2PtCl_4 gave *trans*-$PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_3$, **3**, and $[P(t\text{-}Bu)_3H]_2PtCl_4$, **4**, at room temperature and the novel complex *trans*-$PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_2H$, **5**, upon refluxing. Complex **5** was converted into *trans*-$PtCl_2[P(t\text{-}Bu)_2H]_2$, **6**, upon further heating. Reaction of $P(t\text{-}Bu)_3$ with $PdCl_2$ or Na_2PdCl_4, at room temperature, gave *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2[P(t\text{-}Bu)_3]_2$, **4**; the dinuclear metalated complex $[PdCl\{PCH_2CMe_2(t\text{-}Bu)_2\}]_2$, **5**, was obtained if the reaction mixture was kept at room temperature for 48 h. The hydride *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$, **9**, was obtained when the freshly prepared reaction mixture was heated to ~115 °C for ~30 min.

Introduction

It is now well recognized that platinum metal complexes of bulky phosphines readily undergo intramolecular metalation[1–7] to give cyclometalated complexes usually containing five-membered rings. Another interesting feature of the reactions of bulky phosphines with platinum metal halides is the formation of metal hydrido[8–10] complexes when the reaction is carried out in a protic solvent. Recent work[11] in this laboratory showed that tri-*tert*-butylphosphine undergoes facile intramolecular metalation upon treatment with platinum(II) or palladium(II) chloride in benzene, at room temperature, to give cyclometalated complexes containing four-membered rings. Shaw and co-workers[8,10] obtained the hydrido complexes, $MH_2Cl[P(t\text{-}Bu)_3]_2$ (M = Ir or Rh), from the treatment of the phosphine with hydrated iridium(III) or rhodium(III) chloride in propan-2-ol, at room temperature. In an attempt to prepare the complexes[12] *trans*-$MCl(CO)[P(t\text{-}Bu)_3]_2$ (M = Ir or Rh), reactions of tri-*tert*-butylphosphine with hydrated iridium(III) and rhodium(III) chlorides, in refluxing DMF, were carried out. To our surprise, the reactions resulted in the formation of the complexes, *trans*-$MCl(CO)[P(t\text{-}Bu)_2H]_2$, **1** (M = Ir) and **2** (M = Rh), in quantitative yields. Apart from the expected reduction of the metal, both the reactions involved hitherto unknown elimination of an alkene from the trialkylphosphine ligand. Therefore, reactions of tri-*tert*-butylphosphine with platinum(II) and palladium(II) chlorides were also examined. While this work was in progress, it was reported[13] that the six-coordinate cyclometalated hydrido complex $IrHCl[PCH_2CMe_2(t\text{-}Bu)_2](NC_6H_7)_2$ is formed upon refluxing $P(t\text{-}Bu)_3$ with $[IrCl(COT)_2]_2$ (COT = cyclooctene) and γ-picoline in hexane. The cleavage of phosphorus–phenyl bonds in triphenylphosphine and alkylphenyl tertiary phosphine complexes has been observed by several workers.[14–18] After the completion of this work, a report has also appeared[19] on the formation of diphenylphosphine along with biphenyl, triphenylphosphine, and methyldiphenylphosphine from the decomposition of $Co(CH_3)[PPh_3]_3$. Preliminary results on our investigations on the reactions of tri-*tert*-butylphosphine with iridium(III) and rhodium(III) chlorides have also been reported.[20]

Results and Discussion

Reactions with Iridium(III) and Rhodium(III) Chlorides. The complexes *trans*-$MCl(CO)[P(t\text{-}Bu)_2H]_2$, **1** (M = Ir) and **2** (M = Rh), were obtained in quantitative yields upon refluxing reaction mixtures containing tri-*tert*-butylphosphine and hydrated iridium(III) and rhodium(III) chloride in DMF. The formation of these complexes was accompanied by the evolution of 2-methyl-

(1) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.
(2) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833.
(3) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1972**, *754*, 860.
(4) Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 270.
(5) Jones, C. E.; Shaw, B. L.; Turtle, B. L.; *J. Chem. Soc., Dalton Trans.* **1974**, 992.
(6) Empsall, H. D.; Hyde, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1975**, 1690.
(7) Mason, R.; Textor, M.; Al-Salem, N.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 292.
(8) Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 3679.
(9) Masters, C.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc., Dalton Trans.* **1972**, 664.
(10) Empsall, H. D.; Hyde, E. M.; Mentzer, E.; Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2069.
(11) Goel, R. G.; Montemayor, R. G. *Inorg. Chem.* **1977**, *16*, 2183.
(12) Schuman, H.; Heisler, M.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 1020.
(13) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1977**, *139*, 189.
(14) Mukhedkar, A. J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 947.
(15) (a) Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87; (b) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529.
(16) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2681.
(17) Fahye, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.
(18) Deeming, A. J.; Kimbler, R. E.; Underhill, M.; *J. Chem. Soc., Dalton Trans.* **1973**, 2590.
(19) Michman, M.; Kaufman, V. R.; Nussbaum, S.; *J. Organomet. Chem.* **1979**, *182*, 547.
(20) Goel, R. G.; Montemayor, R. G.; Ogini, W. O. *J. Am. Chem. Soc.* **1978**, *100*, 3629.

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propene which was converted into 1,2-dibromo-2-methylpropane by treatment with bromine; the ^1H NMR spectrum of the resulting brominated product was identical with that of an authentic sample of 1,2-dibromo-2-methylpropane. **1** and **2** were fully characterized by elemental analyses and molecular weight measurements (in benzene) and by ^1H and ^{31}P NMR and infrared spectral measurements. Both the complexes have been prepared previously[21] from the reaction of di-*tert*-butylphosphine with the appropriate iridium(I) and rhodium(I) precursors. The ^1H NMR spectra for **1** and **2** were identical with those reported[21] by previous workers. Their $^{31}P\{^1H\}$ NMR spectra in dichloromethane, at ambient temperature, showed single broad resonances at 76.6 and 80.1 ppm, respectively. At 183 K, a sharp singlet at 72.7 ppm was observed for **1** and a sharp doublet at 77.5 ppm ($^1J_{Rh-P}$ = 115 Hz) was observed for **2**. The infrared spectra for **1** and **2** showed strong bands at 1940 and 1965 cm^{-1}, respectively, due to the CO stretching frequencies. Medium bands at ca. 2360 and 890 cm^{-1}, attributable to the P–H stretching and P–H bending frequencies,[23] respectively, were also present in the spectrum of each complex.

No 2-methylpropene was produced when a solution of tri-*tert*-butylphosphine in DMF was refluxed for 4 h; the ^1H NMR spectrum of the refluxed solution was found to be identical with that of a freshly prepared solution. Thus, the formation of **1** or **2** does not seem to involve prior conversion of $P(t\text{-Bu})_3$ into $P(t\text{-Bu})_2H$ and $H_2C{=}C(CH_3)_2$ as a consequence of its thermal decomposition.

Addition of tri-*tert*-butylphosphine to a suspension of hydrated iridium(III) or rhodium(III) chloride in DMF, at room temperature, gave very dark red solutions which yielded intractable sticky solids which proved very difficult to characterize. The $^{31}P\{^1H\}$ NMR spectra of the dark red solutions showed a strong peak at δ ~44.0 and a few weak peaks downfield from H_3PO_4. The 44.0-ppm resonance is assignable to the phosphonium[20] cation $[P(t\text{-Bu})_3H]^+$ but the assignments for other resonances are not clear at present. The internally metalated tri-*tert*-butylphosphine gives rise to ^{31}P NMR resonance upfield from 85% H_3PO_4. Thus, the presence of cyclometalated complexes in these solutions can be ruled out.

The $^{31}P\{^1H\}$ NMR spectrum of a mixture of $RhCl_3(H_2O)_3$ and 3 mol equiv of $P(t\text{-Bu})_3$ in DMF/C_6D_6, kept at room temperature for 48 h, showed a weak 1:1 doublet at δ 86.5 [^1J(Rh–P) = 112 Hz)], a medium intensity 1:1 doublet at δ 37.0 [^1J(Rh–P) = 115 Hz], and a strong singlet at δ 44.4. Upon heating the reaction mixture to 100 °C the spectrum showed two medium intensity 1:1 doublets, one at δ 156.9 [^1J(Rh–P) = 164 Hz] and the other at δ 100.8 [^1J(Rh–P) = 183 Hz], a medium singlet at δ 63.6, and a strong singlet at δ 47.7. When the mixture was heated to ~140 °C, the spectrum consisted of two singlets at δ 63.0 and 64.1, showing that $P(t\text{-Bu})_3$ does not undergo metalation under these conditions. This is in marked contrast to the reported[13] intramolecular metalation of $P(t\text{-Bu})_3$ in the reaction with $[IrCl(COT)_2]_2$ in the presence of γ-picoline.

The ^1H NMR spectra of the dark red solutions of $MCl_3(H_2O)_3$ (M = Ir or Rh) and $P(t\text{-Bu})_3$ in DMF showed complex resonances in the *tert*-butyl region as well as resonances in the region upfield from Me_4Si. An upfield triplet at −23.86 ppm ($^2J_{P-H}$ = 16 Hz) was observed for the solution from the reaction with iridium(III) chloride. The spectrum of the solution from the reaction with rhodium(III) chloride showed two highfield doublets at −24.52 [^1J(Rh–H) = 5 Hz] and −50.44 [^1J(Rh–H) = 28 Hz] ppm, respectively. By analogy with the reported ^1H NMR data for $IrH_2Cl[P(t\text{-Bu})_3]_2$,[10] the −23.86-ppm triplet can be assigned to a dihydrido species such as $IrH_2Cl[P(t\text{-Bu})_3]_2$(DMF). The −24.52-ppm resonance for the rhodium(III) solution is similar to that reported for $RhH_2Cl[P(t\text{-Bu})_3]_2$, but the observation of another highfield resonance (−50.44 ppm) indicates the presence of another rhodium(III) hydrido species in the solution. Thus, the initial reaction of the phosphine with iridium(III) or rhodium(III) chloride seems to result in the formation of iridium(III) or rhodium(III) hydrido complexes which are converted into **1** or **2** in refluxing DMF.

Reactions with Platinum(II) and Palladium(II) Chlorides. Treatment of the phosphine with platinum(II) chloride or potassium chloroplatinate(II), in DMF, at room temperature, gave the internally metalated complex *trans*-$\overline{PtCl[PC}H_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3$, **3**, and $[P(t\text{-Bu})_3H]_2PtCl_4$, **4**. The reaction is similar to that observed in benzene and can be represented by eq 1. When the

$$6P(t\text{-Bu})_3 + 3PtCl_2 \rightarrow 2\,trans\text{-}\overline{PtCl[PC}H_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3 + [P(t\text{-Bu})_3H]_2PtCl_4 \quad (1)$$

reaction was carried out in refluxing DMF, the novel metalated complex *trans*-$\overline{PtCl[PC}H_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_2H$, **5**, was obtained as the sole platinum-containing species. In another experiment, the reaction mixture was heated to reflux in a closed system for 24 h. This afforded the complex *trans*-$PtCl_2[P(t\text{-Bu})_2H]_2$, **6**, along with some metallic platinum.

Complex **6** had been prepared[21] previously from the reaction of di-*tert*-butylphosphine with sodium tetrachloroplatinate(II). The observed ^1H NMR spectrum for **6** was identical with the reported[21] spectrum. Its $^{31}P\{^1H\}$ NMR spectrum in CH_2Cl_2 at ambient temperature, consisted of a broad central peak and two broad satellite peaks [δ 56.8, ^1J(Pt–P) = 2416 Hz]. At 183 K, each peak was resolved into two peaks clearly showing the presence of two conformers [δ 56.1, ^1J(Pt–P) = 2380 Hz; δ' 50.0, ^1J(Pt–P) = 2382 Hz]. The characteristic infrared bands for **6** include a medium band at 2375 cm^{-1} and strong bands at 860 and 329 cm^{-1} which are assignable to the P–H stretching P–H bending and Pt–Cl stretching frequencies,[23,24] respectively.

The ^1H NMR spectrum of **5** in C_6D_6 exhibited a set of three doublets at δ 1.68 [^3J(P–H) = 12.5 Hz], 1.60 [^3J(P–H) = 12.5 Hz], and 1.55 [^3J(P–H) = 12.5 Hz] in the 3:1:3 intensity ratio, respectively. The two intense peaks are assignable to the *tert*-butyl protons and the less intense peak to the $C(Me)_2$ protons. A few very low intensity peaks due to the CH_2 protons were also evident in the spectrum. Its $^{31}P\{^1H\}$ NMR spectrum in the same solvent showed 12 resonances consisting of two main doublets at 0.75 and 60.2 ppm[^2J(P–P′) = 417 Hz] and eight satellites due to ^{195}Pt–^{31}P spin–spin coupling [^1J(Pt–P) = 2312 and 2836 Hz, respectively]. Thus, the ^{31}P NMR spectrum unequivocally establishes the presence of two nonequivalent phosphorus nuclei, each showing coupling with the ^{195}Pt nucleus as well as with each other. By comparison with the spectra of **3** and **6**, the upfield doublet can be assigned to the metalated phosphine and the downfield doublet to the di-*tert*-butylphosphine. The large value of ^2J(P–P′)

(21) Bright, A.; Mann, B. E.; Masters, C.; Shaw, B. L.; Slade, R. M.; Stainbank, R. E. *J. Chem. Soc. A* **1971**, 1826.
(22) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437 and references therein.
(23) Corbridge, D. E. *Top. Phosphorus Chem.* **1967**, *6*, 235.
(24) Duddel, D. A.; Goggin, P. L.; Goodfellow, R. G.; Norton, M. G.; Smith, J. G. *J. Chem. Soc. A* **1970**, 545 and references therein.

indicates that the two phosphorus nuclei are trans to each other. The infrared spectrum of **5** showed bands due to P–H stretching,[2,3] P–H bending,[23] and Pt–Cl stretching[2,25,26] frequencies at 2370 (medium), 866 (strong), and 265 (very strong) cm^{-1}, respectively. The marked decrease in the Pt–Cl stretching frequency[2,25,26] is consistent with the presence of the Pt–C bond trans to the Pt–Cl bond.

From the aforementioned results it is evident that in refluxing DMF **3** as well as **4** are converted into **5** which, upon further heating, is converted into **6**. The conversion of **4** into **5** most likely involves initial formation of *trans*-$PtCl_2[P(t\text{-}Bu)_3]_2$ which is not isolable and is rapidly converted into **3**. Conversion of **3** into **5** requires elimination of 2-methylpropene from either the coordinated $P(t\text{-}Bu)_3$ or the cyclometalated phosphine. A plausible reaction pathway could be elimination of $CH_2{=}C(CH_3)_2$ from the cyclometalated phosphine and rapid conversion of the resulting phosphido complex $PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3$ into 5 (eq 2). Unfortunately, the appropriate isotopically

$$trans\text{-}PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_3 \rightarrow PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3 + CH_2{=}C(CH_3)_2 \quad (2a)$$

$$PtCl[P(t\text{-}Bu)_2]P(t\text{-}Bu)_3 \rightarrow trans\text{-}PtCl[P(t\text{-}Bu)_2H][PCH_2CMe_2(t\text{-}Bu)_2] \quad (2b)$$

labeled precursors, required to verify the proposed reaction pathway, are not easily accessible. Furthermore, phosphido derivatives of the type implicated in reaction 2 are also not known. The $^{31}P\{^1H\}$ spectrum of a mixture of $PtCl_2$ and $P(t\text{-}Bu)_3$ (1:3 mole ratio) in DMF/C_6D_6, heated to 100 °C for 12 h, showed characteristic resonances due to **3** and a broad resonance at ca. δ 60.5 which can be attributed to excess $P(t\text{-}Bu)_3$. Further heating to 140 °C caused complete conversion of **3** into **5** as shown by the $^{31}P\{^1H\}$ NMR data.

Conversion of **5** into **6** involves cleavage of the Pt–C bond as well as a P–C bond of the cyclometalated phosphine as represented by eq 3.

$$trans\text{-}PtCl[PCH_2CMe_2(t\text{-}Bu)_2]P(t\text{-}Bu)_2H + HCl \xrightarrow{\Delta} trans\text{-}PtCl_2[P(t\text{-}Bu)_2H]_2 + CH_2{=}C(CH_3)_2 \quad (3)$$

Although it has been reported that the Pt–C bond in $PtCl[CHMeC_6H_4PPh_2]P(o\text{-vinylphenyl})Ph_2$ can be cleaved by HCl, most of the cyclometalated platinum(II) complexes of the type PtCl(P–C)L, where (P–C) is a metalated phosphine and L is unmetalated phosphine, are reported to be remarkably stable. For example, it has been reported that the complex *trans*-$PtCl[C_6H_3MeP(t\text{-}Bu)_2]P(t\text{-}Bu)_2(p\text{-tolyl})$[2] is recovered unchanged after remaining molten at ca. 200 °C for 30 min and the complexes *trans*-$PtCl[CH_2C_6H_4PPh(o\text{-tolyl})]PPh(o\text{-tolyl})_2$,[2] *trans*-$PtCl[CH_2C_6H_4P(t\text{-}Bu)(o\text{-tolyl})]P(t\text{-}Bu)(o\text{-tolyl})_2$,[3] and *trans*-$PtCl[C_6H_4P(t\text{-}Bu)_2]P(t\text{-}Bu)_2Ph$[2] remain unchanged upon treatment with HCl. There seems to be no precedent for the reactions involved in the conversion of **3** into **5** as well as its subsequent conversion into **6**.

The dinuclear complex, $Pd_2Cl_2(\mu\text{-}Cl)_2\{P(t\text{-}Bu)_3\}_2$, **7**, the metalated dinuclear complex, $[PdCl\{PCH_2CMe_2(t\text{-}Bu)_2\}]_2$, **8**, or the hydrido complex, *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$, **9**, were obtained from the reaction of tri-*tert*-butylphosphine with palladium(II) chloride or potassium or sodium chloropalladate, depending upon the reaction temperature and reaction time. Complex **7** was obtained as the sole palladium-containing species when the phosphine and palladium(II) chloride were stirred in DMF at room temperature for ~1 h. When the reaction mixture was stirred for ~48 h, the metalated dinuclear complex, **8**, was obtained in almost quantitative yield. When the reaction mixture was heated to ~115 °C for ~30 min, most of the palladium(II) was converted into the hydrido complex, **9**. Heating the reaction mixture to reflux resulted in the reduction of the palladium(II) to the metallic form.

The ^1H NMR spectrum of a freshly prepared solution of **7** in CH_2Cl_2 showed a doublet at 1.35 ppm [^3J(P–H) = 14.8 Hz], and its $^{31}P\{^1H\}$ NMR spectrum in the same solvent showed a single resonance at 121.3 ppm. The infrared spectrum of the freshly prepared **7**, in the solid state, showed a strong band at 340 cm^{-1} due to the terminal Pd–Cl stretching frequency[24] and medium and strong bands at 315 and 248 cm^{-1} due to the bridging Pd–Cl stretching modes.[24] The ^1H and $^{31}P\{^1H\}$ NMR spectra as well as the infrared spectrum of **7** were identical with that observed for an authentic sample of *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2[P(t\text{-}Bu)_3]_2$ prepared[28] by the treatment of *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2[As(t\text{-}Bu)_3]_2$ with $P(t\text{-}Bu)_3$. The dimeric nature of **8** was confirmed by molecular weight determination in benzene. Its ^1H NMR spectrum in dichloromethane showed a set of three doublets at 1.60 [^3J(P–H) = 13.5 Hz], 1.56 [^3J(P–H) = 14 Hz), and 1.48 [^3J(P–H) = 14 Hz] ppm in the intensity ratio of 1:9:3, respectively, and its ^{31}P NMR spectrum in the same solvent showed a single resonance at −11.9 ppm. The infrared spectrum of **8** showed strong bands at 237 and 225 cm^{-1} which can be attributed to the stretching of the bridging Pd–Cl bonds.[24] The ^1H and ^{31}P NMR and infrared spectra of **9** were identical with those of an authentic sample of *trans*-$PdHCl\{P(t\text{-}Bu)_3\}_2$ prepared by the previously reported method.[29]

Previous work[11] has shown that treatment of 2 mol equiv of $P(t\text{-}Bu)_3$ with $PdCl_2(COD)$ or $PdCl_2(C_6H_5CN)_2$ results in the formation of *trans*-$PdCl_2[P(t\text{-}Bu)_3]_2$, **10**, which, unlike the analogous platinum(II) derivative, has been isolated and found to behave as a molecular species in benzene. The isolation of **7** instead of **10** in the present work seems to indicate that the equilibrium represented by eq 4 lies to the right in DMF. An investigation[28] on the

$$2\,trans\text{-}PdCl_2[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}Pd_2Cl_2(\mu\text{-}Cl)_2[P(t\text{-}Bu)_3]_2 + 2P(t\text{-}Bu)_3 \quad (4)$$

preparation and characterization of authentic samples of **7** showed that it readily undergoes intramolecular metalation in solution as well as in the solid state to give **8**. However, in the present work, complex **8** is not solely derived from the intramolecular metalation reaction of **7** (vide infra).

The $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared mixture of $PdCl_2$ and $P(t\text{-}Bu)_3$ (1:3 mole ratio), in DMF/C_6D_6, showed a strong resonance (δ 122.7) due to **7**, a weaker resonance (δ 81.9) due to **9**, and a broad resonance at δ 63.0 which can be attributed to excess phosphine. When the mixture was heated to 70–100 °C, the resonance due to **7** disappeared completely, the resonance due to **9** increased in intensity, and the resonance at δ 63.0 remained unchanged, but a relatively strong new resonance appeared at δ 43.2. There can be little doubt that the δ 43.2 resonance is due to the protonated phosphine. The spectral data suggest that the initial product of the reaction of $P(t\text{-}Bu)_3$ with $PdCl_2$ in DMF is **7** which is rapidly con-

(25) Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2801.
(26) Adams, D. M.; Chatt, J.; Gerratt, J.; Westland, A. D. *J. Chem. Soc.* **1964**, 734.
(27) Brookes, P. R.; Nyholm, R. S. *J. Chem. Soc., Chem. Commun.* **1970**, 169.
(28) Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *Inorg. Chem.*, **1981**, *20*, 3611.
(29) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.

verted into **9** with concomitant protonation of approximately 50% of the phosphine present in the system. Further heating of the mixture to ~120 °C resulted in the disappearance of the resonance due to protonated phosphine with a concomitant increase in the intensity of the resonance due to **9** From these observations it appears that the conversion of **7** into **9** is accompanied by the formation of the phosphonium salt, $[P(t\text{-Bu})_3H]_2PdCl_4$, which is converted into **9** at ~120 °C.

The reaction of $P(t\text{-Bu})_3$ with commercially available $PdCl_2$, in hot DMF, discovered in the present work provides a very convenient method of preparation of *trans*-$PdHCl[P(t\text{-Bu})_3]_2$ which has hitherto been obtained[29,30] from the oxidative addition of HCl to $Pd[P(t\text{-Bu})_3]_2$[31] which is not easily accessible. The ^1H NMR spectrum of a solution of **9** in DMF, kept at room temperature for 48 h, showed no resonance upfield from Me_4Si; the 1:2:1 *tert*-butyl triplet observed for **9** was replaced by a complex multiplet. The spectral changes clearly indicate conversion of **9** into the internally metalated complex, *trans*-$PdCl[PCH_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3$, **11**, as represented by eq 5.

$$trans\text{-}PdHCl[P(t\text{-Bu})_3]_2 \rightarrow trans\text{-}PdCl[PCH_2CMe_2(t\text{-Bu})_2]P(t\text{-Bu})_3 + H_2 \quad (5)$$

It was also found that the complexes **11** and **8** are readily interconvertible through a solvent dependent equilibrium represented by eq 6. Thus, the formation of **8** as the sole

$$2\,trans\text{-}PdCl[PCH_2CMe(t\text{-Bu})_2]P(t\text{-Bu})_3 \rightarrow [PdCl\{PCH_2CMe_2(t\text{-Bu})_2\}]_2 + 2P(t\text{-Bu})_3 \quad (6)$$

palladium(II)-containing species in the reaction mixture, kept at room temperature for 48 h, seems to involve a sequence of reactions. The spectral evidence suggests that complex **8** is derived mainly from **9** which undergoes intramolecular metalation to give **11** which is subsequently converted into **8**.

In summary, the course of the reaction of $P[t\text{-Bu})_3$ with the four platinum metals included in this investigation is markedly dependent upon the nature of the metal, and, for the given metal, upon the conditions of the reaction. All of the reactions examined in the present work give unexpected products. The reactions involving elimination of $CH_2{=}C(CH_3)_2$ and quantitative formation of the complexes containing $P(t\text{-Bu})_2H$ are without precedent and represent an hitherto unrecognized pathway for relieving steric crowding in metal complexes of bulky phosphines.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of oxygen-free dry nitrogen by using either a drybox (Vacuum Atmosphere Corp. Dri-Lab equipped with a Model HE-493 Dri-Train) or Schlenk-tube and vacuum-line techniques. Tri-*tert*-butylphosphine was prepared as described previously,[11] and its purity was checked by ^1H and ^{31}P NMR spectral measurements. Platinum metal salts were used as received from Johnson Matthey and Mallory Ltd. Reagent grade dimethylformamide (DMF) was stored over molecular sieves prior to use. Other solvents were purified by standard methods. Reactions were monitored periodically by recording the NMR spectra of reaction mixtures sealed in NMR tubes.

Physical Measurements. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, AZ, by Galbraith Laboratories, Knoxville, TN, or By Guelph Chemical Laboratory, Guelph, Ontario. Molecular weights were determined on benzene solutions with Hitachi Perkin-Elmer 115 osmometer. Infrared spectra were obtained with a Perkin-Elmer 180 spectrometer using samples prepared as mulls in Nujol or halocarbon oil and pressed between KRS or polyethylene windows. ^1H NMR spectra were recorded either on a Varian A-60 and a HA-100 spectrometer or on a Bruker WP-60 FT spectrometer using solvent chemical shifts as internal reference; the reported chemical shifts are relative to internal Me_4Si. $^{31}P\{^1H\}$ spectra were measured with a Bruker WP- 60FT spectrometer using 85% H_3PO_4 as external reference; positive chemical shifts are downfield from 85% H_3PO_4. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

Reactions of Tri-*tert*-butylphosphine with Iridium(III) and Rhodium(III) Chlorides. (a) $P(t\text{-Bu})_3$ (2–3 mmol) was added to a suspension or $IrCl_3{\cdot}3H_2O$ or $RhCl_3{\cdot}3H_2O$ (1 mmol) in dimethylformamide (25 mL), and the dark red suspension was stirred at room temperature for 3 h to give a dark reddish solution. Removal of the solvent gave dark sticky solids which could not be characterized.

(b) $P(t\text{-Bu})_3$ (3 mmol) was added to a suspension of $RhCl_3{\cdot}3H_2O$ or $IrCl_3{\cdot}3H_2O$ (1 mmol) in a two-necked flask fitted with a condenser on one neck and a source of oxygen-free dry nitrogen on the other. The top of the condenser was connected in series to a distilled water scrubber, a U-tube containing anhydrous calcium chloride, a flask containing 0.2 M solution of bromine in carbon tetrachloride, and a mercury bubbler. The suspension was refluxed, under nitrogen, with stirring, for 5 h to give a clear yellow solution, and the system was then flushed thoroughly with nitrogen. The reaction mixture was cooled to room temperature, concentrated in vacuo to half its volume, and then cooled in an ice-bath. Addition of cold methanol (40 mL) to the cold reaction mixture gave a yellow crystalline solid which was recrystallized from hexane; yields ~95%. Anal. Calcd for $Ir(CO)Cl[P(t\text{-Bu})_2H]_2$: C, 38.00; H, 7.08; Cl, 6.64; P, 11.50; mol wt 458. Found: C, 37.94; H, 7.08; Cl, 7.00; P, 11.00; mol wt 433 (in benzene) [mp 270 °C]. Calcd for $Rh(CO)Cl[P(t\text{-Bu})_2H]_2$: C, 44.50; H, 8.30; Cl, 7.80; P, 13.50; mol wt 547. Found: C, 44.00; H, 8.60; Cl, 8.00; P, 13.50; mol wt 520 (in benzene) [mp 265 °C]. ^1H NMR (in $CDCl_3$ at −30 °C): *trans*-$IrClCO[P(t\text{-Bu})_2H]_2$, δ(P–C–C–H) 1.46 [q, ^3J(P–H) + ^5J(P–H) = 14.3 Hz], *trans*-$RhClCO[P(t\text{-Bu})_2H]_2$, δ(P–C–C–H) 1.44 [q, ^3J(P–H) + ^5J(P–H) = 14.8 Hz]; δ(P–H) 4.11 ppm [^1J(P–H) = 347 Hz]. The bromine solution was found to be partially decolorized and its ^1H NMR spectrum was found to be identical with that of an authentic solution of 1,2-dibromo-2-methylpropane in carbon tetrachloride prepared according to the literature procedure.

Reaction of Tri-*tert*-butylphosphine with Potassium Tetrachloroplatinate(II). (a) $P(t\text{-Bu})_3$ (3 mmol) was added to 25 mL of DMF containing 1 mmol of K_2PtCl_4, and the mixture was stirred at room temperature for 24 h to give an orange solution containing an off-white suspension. After the solvent was removed in vacuo, the residue was extracted with hexane to give 0.61 mmol of hexane-soluble *trans*-$PtCl[PCH_2C(CH_3)_2(t\text{-Bu})_2]P(t\text{-Bu})_3$. Anal. Calcd for $PtCl[PC_4H_5(t\text{-Bu})_2]P(t\text{-Bu})_3$: C, 45.44; H, 8.43; Cl, 5.58. Found: C, 45.50; H, 8.52; Cl, 5.60. ^1H NMR (C_6D_6): $\delta[P(t\text{-Bu})_3]$ 1.56 [d, ^3J(P–H) = 11.5 Hz]; $\delta[P(t\text{-Bu})_2]$ 1.62 [d, ^3J(P–H) = 12.4 Hz]; $\delta(PCMe_2)$ 1.48 [d, ^3J(P–H) = 12.7 Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6) $\delta[P(t\text{-Bu})_3]$ 66.8 ppm [J^{195}(Pt–P) = 2680 Hz], $\delta[P(t\text{-Bu})_2CMe_2CH_2]$ −12.8 ppm [^1J(Pt–P) = 2360 Hz, ^2J(P–P′) = 382 Hz]. The hexane-insoluble solid was extracted with dichloromethane to give 0.3 mmol $\{P(t\text{-Bu})_3H\}_2PtCl_4$. Anal. Calcd for $[P(t\text{-Bu})_3H]_2PtCl_4$: C, 38.75; H, 7.60; Cl, 19.06. Found: C, 38.70; H, 7.80; Cl, 18.49 [Λ_M = 132 Ω^{-1} cm^2 mol^{-1} (~10^{-3} M solution in nitromethane)]. ^1H NMR (CH_2Cl_2): δ(P–C–C–H) 1.80 [d, ^3J(P–H) = 15.0 Hz]; δ(P–H) 7.40 [d, ^1J(P–H) = 464 Hz]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.0 (s).

(b) A mixture of $P(t\text{-Bu})_3$ (3 mmol) and K_2PtCl_4 or $PtCl_2$ (1 mmol) in DMF (25 mL) was refluxed for 3 h. After the solvent was removed in vacuo, the resulting solid was extracted with hexane to give a white solid which was recrystallized from hexane; mp 180 °C. Anal. Calcd for $PtCl[P(t\text{-Bu})_2CMe_2CH_2]P(t\text{-Bu})_2H$: C, 41.45; H, 7.78; Cl, 6.14; mol wt 579. Found: C, 41.52; H, 7.83; Cl, 6.38; mol wt 582 (benzene) [yield 95%].

(c) A mixture of K_2PtCl_4 (2 mmol) and $P(t\text{-Bu})_3$ (6 mmol) in DMF (30 mL) was refluxed in a closed system for 48 h. The

(30) Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803.
(31) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5050.

solvent was removed in vacuo, and the residue was extracted with hexane to give an off-white solid which was recrystallized from the same solvent to give a white solid; mp 280 °C dec. Anal. Calcd for $PtCl_2[P(t\text{-}Bu)_2H]_2$: C, 34.53; H, 6.83; Cl, 12.77; mol wt 558. Found: C, 34.94; H, 6.93; Cl, 11.90; mol wt 556 (benzene) [yield 60%]. ^1H NMR ($CDCl_3$): δ(P–C–C–H) 1.60 [q, ^3J(P–H) + ^5J(P–H) = 14.2 Hz].

Reactions of Tri-*tert*-butylphosphine with Palladium(II) Chloride or Sodium Tetrachloropalladate. (a) $P(t\text{-}Bu)_3$ (3 mmol) was added to DMF (25 mL) containing Na_2PdCl_4 (1 mmol), and the mixture was stirred for 48 h to give a yellowish solution. The solution was filtered, and the solvent was removed in vacuo to give a yellow solid which was washed with cold ethanol (20 mL) and recrystallized from a mixture of benzene and hexane to give a yellow crystalline solid; mp 210 °C dec. Anal. Calcd for $[PdCl\{P(t\text{-}Bu)_2CMe_2CH_2\}]_2$: C, 42.24; H, 7.59; Cl, 10.36; mol wt 685. Found: C, 42.17; H, 7.85; Cl, 9.98; mol wt 694 (benzene) [yield 75%].

(b) A mixture of $P(t\text{-}Bu)_3$ (3 mmol) and $PdCl_2$ or Na_2PdCl_4 (1 mmol) in DMF (25 mL) was heated, with stirring, in an oil bath. As the temperature approached 100 °C, the reddish colour of the solution began to change to green. At 115 °C the solution became dark green when it was cooled to room temperature to give some greenish white solid. More solid was obtained upon concentrating the solution. Filtration and recrystallization of the solid from a mixture of benzene and hexane gave pure *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$ in 90% yield; mp 146 °C. Anal. Calcd for $PdHCl[P(t\text{-}Bu)_3]_2$: C, 52.70; H, 10.06; mol wt 547. Found: C, 52.37, H, 10.19; mol wt 550 (benzene). ^1H NMR (C_6D_6):(δ[P(C–C–H)] 1.5 [t, ^3J(P–H) + ^5J(P–H) = 12.3 Hz]; δ(Pd–H) −18.3 [t, ^2J(P–H) = 12.3 Hz]. $^{31}P\{^1H\}$NMR (C_6D_6): δ 81.7 (s). IR (Nujol mull): ν(Pd–H) 2215, ν(Pd–H) 766, ν(Pd–Cl) 255 cm^{-1}.

Acknowledgment. Financial assistance of the Natural Sciences and Engineering Research Council, Canada, is gratefully acknowledged.

Registry No. 1, 33246-91-2; 2, 33246-87-6; 3, 63230-78-4; 4, 63230-82-0; 5, 80662-59-5; 6, 34721-30-7; 7, 77932-99-1; 8, 69393-58-4; 9, 63166-71-2; 11, 63230-80-8.

Dehydrogenation of Alcohols and Hydrogenation of Aldehydes Using Homogeneous Ruthenium Catalysts

Chu W. Jung and Philip E. Garrou*

Dow Chemical USA, Central Research-New England Laboratory, Wayland, Massachusetts 01778

Received October 21, 1981

A series of ruthenium(II) diphosphine hydrides of the type $RuH_2(CO)(PPh_3)(L\text{–}L)$ (I) where L–L = $Ph_2Ph(CH_2)_nPPh_2$ (n = 1–4), $Ph_2P(CH_2)_2AsPh_2$, and 1,2-$(Ph_2P)_2C_6H_4$ have been prepared and reacted with trifluoroacetic acid ($HOAc_F$) to yield complexes $Ru(OAc_F)_2CO(PPh_3)_m(L\text{–}L)$ where L–L = 1,2-$(PPh_2)_2C_6H_4$ (m = 0, 1), $PPh_2CH_2CH_2AsPh_2$ (m = 1), and $(Ph_2P)_2(CH_2)_n$ (n = 3, 4; m = 0). These complexes have been extensively characterized by ^1H, ^{31}P, and ^{19}F NMR spectroscopy and most of their stereochemistries unambiguously determined. The catalytic activities and lifetimes of these new complexes in alcohol dehydrogenation and ketone hydrogenation were examined and compared to those of of $Ru(OAc_F)_2CO(PPh_3)_2$ (IIa). In contrast to past reports, we find that IIa when used as a dehydrogenation catalyst deactivates due to its tendency to decarbonylate the product aldehydes. Phosphorus-31 NMR analyses reveal that IIa reacts with heptanal to yield $Ru(OAc_F)_2(CO)_2(PPh_3)_2$ (10% conversion in 30 min at 100 °C). While the diphosphine trifluoroacetate complexes are more active than IIa, they also deactivate by decarbonylation of the product aldehyde or ketone. These new diphosphine complexes are also more efficient hydrogenation catalysts than IIa.

Introduction

Dobson and Robinson[1,2] and more recently Rybak and Ziolkowski[3] have described their extensive studies into (trifluoroacetato)ruthenium(II) alcohol dehydrogenation catalysts and their polystyrene supported analogues, respectively. The mechanism originally proposed by Robinson[1] (Scheme I) requires an isomerization whereby the mutually trans phosphine ligands of intermediate **i** must rearrange to a cis configuration (isomer **j**) in order to complete the catalytic cycle. We felt that initially locking the phosphines into a cis configuration by means of a chelating diphosphine (L–L) could affect the rate of the overall reaction if the **i** → **j** rearrangement was involved in the rate-determining step of the overall catalytic sequence. We therefore now wish to report on a series of ruthenium(II) trifluoroacetate diphosphine complexes that we have prepared and compare their catalytic activity to that previously found for $Ru(OAc_F)_2CO(PPh_3)_2$. Products have been characterized by analytical and spectroscopic methods, and where possible, their stereochemistry has been assigned.

Experimental Section

Unless indicated otherwise, all operations were conducted under purified argon or nitrogen, using standard inert atmosphere techniques.[4]

Infrared spectra were determined on a Beckman IR4240 spectrometer. NMR spectra were recorded on a JEOL FX90-Q spectrometer equipped with a broad-band, tunable probe. A Bruker WM250 spectrometer was used to measure 250-MHz ^1H NMR spectra. Phosphorous-31 and ^{19}F chemical shifts were referenced to external 85% H_3PO_4 and internal C_6F_6, respectively. The latter chemical shifts were converted to the δ_{CFCl_3} scale by using the relationship $\delta_{CFCl_3} = -162.28 + \delta_{C_6F_6}$.

(1) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 137.
(2) Robinson, S. D. British Patent 1530447, Nov 1, 1978.
(3) Rybak, W. K.; Ziolkowski, J. J. *J. Mol. Catal.* **1981**, *11*, 365.
(4) Shriver, D. F., "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

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