Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of $[Rh_2(CO)_3$-$Cl(DPM)_2]^+$ (left) and $[Rh_2(CO)_2Cl(DPM)_2]^+$ (right) in CD_2Cl_2 under N_2 at selected temperatures.
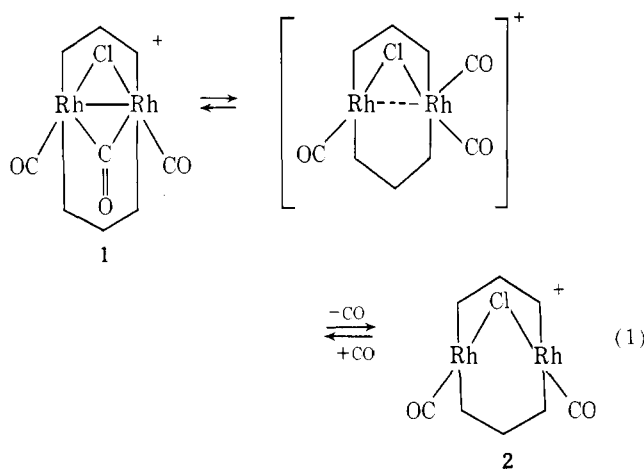
the results of a crystal structure analysis of **3** now in progress. The arsine analogue of **3** is prepared similarly.

$[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(DPM)_2]^+$ can also be obtained as the $[Rh(CO)_2Cl_2]^-$ salt (**4**) from a 50% excess of $[Rh_2(CO)_4Cl_2]$ or $[Rh_2Cl_2(c\text{-}C_8H_{12})_2]$ under CO. By this route, $[Ir_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(DPM)_2][Ir(CO)_2Cl_2]$ (**5**) can be obtained from the analogous iridium(I) precursors. Complex **5** shows $\nu_{C\equiv O}$ for the cation at 2000 (sh) 1993 (vs), and 1843 (m) cm^{-1}. The anion shows $\nu_{C\equiv O}$ at 2058 (m) and 1982 (s) cm^{-1}. The conductivity of 84 Ω^{-1} cm^2 equiv^{-1} in acetone indicates it to be a 1:1 electrolyte.

Figure 2 shows the $^{31}P\{^1H\}$ NMR spectrum obtained from a solution of **1** in CD_2Cl_2 under N_2. The 233 K spectrum shows two complex, second-order patterns attributable to **1** (δ 26.0 ppm vs. external H_3PO_4) and **2** (δ 15.4 ppm), respectively.[12] The presence of **2** is consistent with the ready loss of CO from **1**. On warming, rapid CO exchange between **1** and **2** appears to occur. The spectrum of **1** has been successfully analyzed as an AA'A''A'''XX' system with $^1J_{Rh-P}$ = 118.3 Hz, $^2J_{Rh-P}$ = -24.1 Hz and $|^1J_{Rh-Rh}|$ = 127.8 Hz. The analysis of the spectrum of **2** is less satisfactory because of the near coincidence of many of the weaker lines. However the close resemblance to the $^{31}P\{^1H\}$ spectrum of $[Rh_2(CO)_2Cl_2(DPM)_2]$[13]

indicates that the metal-metal interaction in **2** should be similar to that proposed for this neutral dimer.[10] Support for this comes from the electronic spectrum of **2** which shows an analogous "proximity shifted" band at 443 nm (CH_2Cl_2 solution) which is absent in the spectrum of **1**. Complex **2** thus presents an interesting contrast to $[Pd_2Cl_2(DPM)_2]$[9] in that addition of the bridging carbonyl leads to the formation of a metal-metal bond.

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(12) Confirmed by independent measurements on **1** under CO and **2** under N_2.
(13) In **2** the separation of the major peaks ($|^1J_{Rh-P} + ^2J_{Rh-P}|$) is 113.0 Hz while for $[Rh_2(CO)_2Cl_2(DPM)_2]$ the resonance is centered at δ 16.0 ppm with $|^1J_{Rh-P} + ^2J_{Rh-P}|$ = 114.0 Hz.

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An Unusual Reaction of Tri-*tert*-butylphosphine with Rhodium(III) and Iridium(III) Chlorides

Sir:

Recent studies[1] demonstrate that tertiary phosphines containing bulky substituents on phosphorus often form unusual products with transition metals. For example, the hydrido complexes[2,3] $[(t\text{-Bu})_3P]_2MH_2Cl$, where M = Rh or Ir are obtained from the reactions of tri-*tert*-butylphosphine with hydrated iridium(III) and rhodium(III) chlorides. Recently, we found[4] that tri-*tert*-butylphosphine undergoes a facile reaction with platinum(II) and palladium(II) chlorides to form the internally metallated complexes of the type $[(t\text{-Bu})_2$-$PC(CH_3)_2CH_2]M[(t\text{-Bu})_3P]Cl$ (where M = Pt or Pd). The formation of internally metallated hydrido complex $[(t\text{-Bu})_2PC(CH_3)_2CH_2]IrHCl(NC_6H_7)_2$ by the reaction of

(t-Bu)$_3$P with [(COT)$_2$IrCl]$_2$ (COT = cyclooctene) in the presence of γ-picoline has also been reported[5] very recently. In contrast, with less bulky phosphines which form highly reactive two-coordinate platinum(0) and palladium(0) complexes, tri-*tert*-butylphosphine is reported to form rather inert two-coordinate complexes[6-8] with platinum(0) and palladium(0). Herein we wish to report a novel reaction of tri-*tert*-butylphosphine with hydrated rhodium(III) and iridium(III) trichlorides in which a P–C bond of (t-Bu)$_3$P is cleaved and the complexes *trans*-[(t-Bu)$_2$HP]RhClCO (**1**) and *trans*-[(t-Bu)$_2$HP]$_2$IrCl(CO) (**2**) are formed in almost quantitative yields.

When a mixture of RhCl$_3$(H$_2$O)$_3$ (1 mmol) and (t-Bu)$_3$P (5 mmol) was refluxed in dimethylformamide (DMF), under nitrogen, a dark red solution with some suspended solid was formed, initially. After 30 min, a clear yellow solution was obtained which was refluxed for another 2 h. Upon cooling the yellow solution to room temperature and adding methanol, **1** was obtained as a yellow solid in 95% yield, mp 265 °C. A similar reaction of (t-Bu)$_3$P with IrCl$_3$(H$_2$O)$_3$ afforded **2** in over 95% yield, mp 270 °C. Both **1** and **2** were characterized by elemental analyses (C, H, Cl, P, Rh, and Ir) and by molecular weight and infrared and NMR spectral measurements. Conductance measurements on 10^{-3} M solutions in nitromethane showed that both **1** and **2** are nonelectrolytes. The molecular weights for **1** and **2** in benzene were found to be 433 and 520, respectively. The infrared spectra of both compounds showed medium-intensity bands at ~2360 and 890 cm^{-1} due to the P–H stretching and P–H bending frequencies,[9] respectively. The CO stretching frequency for **1** and **2** was observed at 1965 and 1940 cm^{-1}, respectively. The ^{31}P NMR spectrum of **1**, in dichloromethane, at −90 °C, showed a doublet (δ 77.5 ppm downfield from external H$_3$PO$_4$, $J_{\text{P-Rh}}$ = 115 Hz), and the ^{31}P NMR spectrum of **2** showed a single peak (δ 72.7 ppm downfield from external H$_3$PO$_4$). Both **1** and **2** have been prepared previously[10] from the reactions of (t-Bu)$_2$Ph following usual preparative methods. The ^{1}H NMR spectra for both compounds, at ambient temperature as well as at low temperatures, were identical with those reported by previous workers.[10]

While the cleavage of P–C bond in the reactions of tertiary phosphines with transition metals leading to the formation of phosphido complexes is well recognized,[11-13] the present report provides the first example of a P–C bond cleavage reaction of a tertiary phosphine resulting in the formation of a secondary phosphine complex. The formation of **1** and **2** was accompanied by the evolution of H$_2$C=C(CH$_3$)$_2$ which was trapped as H$_2$BrC—CBr(CH$_3$)$_2$ and characterized by its ^{1}H NMR spectrum. No H$_2$C=C(CH$_3$)$_2$ was evolved when a solution of (t-Bu)$_3$P in dimethylformanide was refluxed for 3 h. Therefore, the formation of **1** and **2** does not appear to involve the prior formation of (t-Bu)$_2$PH as a consequence of thermal decomposition of (t-Bu)$_3$.

^{1}H NMR measurements on solutions of RhCl$_3$(H$_2$O)$_3$ or IrCl$_3$(H$_2$O)$_3$ and tri-*tert*-butylphosphine (1:5 mole ratio), in *N,N*-dimethylformamide, indicated the presence of hydrido complexes. The ^{1}H NMR spectra for both rhodium and iridium solutions showed a complex multiplet due to the *tert*-butyl protons. For the rhodium solution, two high-field doublets were observed at δ −24.52 ($^1J_{\text{Rh-H}}$ = 5 Hz) and −50.44 ($^1J_{\text{Rh-H}}$ = 28 Hz) ppm, respectively. By analogy to the ^{1}H NMR data for the reported rhodium(III) hydrido complexes,[2] the doublet at −24.52 ppm can be due to a six-coordinate monohydrido species RhHCl$_2$[(t-Bu)$_3$P]$_x$(DMF)$_y$ and the doublet at −50.44 ppm can be due to the pentacoordinate species RhHCl$_2$[(t-Bu)$_3$P]$_x$(DMF)$_y$. The failure to observe the splittings due to the P–H spin-spin coupling is not unusual and can be explained in terms of rapid phosphine exchange within each complex. The ^{1}H NMR spectrum of the iridium solution

showed a triplet at δ −23.86 ppm ($^2J_{\text{P-H}}$ = 16 Hz). By comparison with the ^{1}H NMR data for [(t-Bu)$_3$P)]$_2$IrH$_2$Cl$_3$,[3] the observed triplet can be associated with a six-coordinate dihydrido complex [(t-Bu)$_3$P]$_2$IrH$_2$Cl(DMF). Thus, there can be little doubt that the formation of **1** or **2** is preceded by the formation of rhodium(III) or iridium(III) hydrido complexes. However, attempts to isolate the hydride species by precipitation or removal of the solvent and excess phosphine were not successful owing to the formation of oily materials. No evidence for the presence of metallated phosphine[14] in the above solutions was obtained in the ^{31}P NMR spectrum. Further investigations on the reactions of tri-*tert*-butylphosphine with platinum metals are in progress.

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A Model β Turn. Circular Dichroism and Infrared Spectra of a Tetrapeptide[1]

Sir:

Circular dichroism (CD) measurements have been used extensively to evaluate the conformation of proteins and polypeptides in solution.[2-4] For accurate determinations of conformation, the optical parameters of all known secondary structures must be known. The evaluation of conformation of proteins to date has been based on the α-helical, β sheet and random conformational optical parameters deduced from either synthetic polypeptides,[2] or from five proteins of known structure.[3] However, the β turn has been neglected because the parameters were unknown, although the β turn or β bend has been recognized as playing an important role in globular proteins:[5] the average frequency of amino acid residues in β turns is 32%.[9]

The β turn is a structural feature involving four consecutive residues where the polypeptide chain folds back on itself, with hydrogen bonding between the CO group of the first residue and the NH group of the 4th residue. Only recently have the exact parameters been evaluated for the various types of β turns,[5a,c,6] their presence tabulated in proteins,[5] and their optical activity theoretically evaluated.[7] β bends have been classified into 11 types,[5a,c] but types I and II are found most