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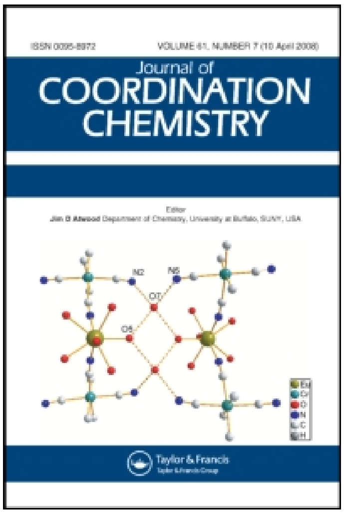

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FACILE INTERMOLECULAR PHOSPHINE LIGAND EXCHANGE REACTIONS BETWEEN SQUARE PLANAR IRIDIUM AND PLATINUM CENTERS

Robert L. Rominger[a]; Jeffrey M. McFarland[a]; James R. Jeitler[a]; Jeffrey S. Thompson[a]; Jim D. Atwood[a]
[a] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York, USA

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FACILE INTERMOLECULAR PHOSPHINE LIGAND EXCHANGE REACTIONS BETWEEN SQUARE PLANAR IRIDIUM AND PLATINUM CENTERS

ROBERT L. ROMINGER, JEFFREY M. McFARLAND, JAMES R. JEITLER, JEFFREY S. THOMPSON and JIM D. ATWOOD*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214, USA

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Reactions between square planar complexes, trans-$Ir(CO)(R)L_2$ (R = Cl, Me; L = PPh_3, $P(p\text{-tolyl})_3$, $PMePh_2$), trans-$Pt(Cl)(H)L'_2$ (L' = PPh_3, $P(p\text{-tolyl})_3$, PEt_3), cis-$Pt(Cl)_2L'_2$ and trans-$Pt(Cl)_2(PEt_3)_2$, result in intermolecular exchange of phosphine ligands. Exchange between two iridium complexes is facile; exchanges between iridium and platinum complexes or between two platinum complexes occur with half-lives of hours. The reactions are followed by ^{31}P NMR. The reactions are best interpreted as phosphine ligand dissociation with dissociation from iridium occurring more readily than from platinum. The observed phosphine dependence on the rate, L = $P(p\text{-tolyl})_3 > PPh_3 > PEt_3$ is consistent with a dissociative process. The dissociated phosphine then causes an associative substitution with the other complexes. Associative substitution on square planar iridium(I) complexes are known to occur much more readily than on square planar platinum(II) complexes.

KEYWORDS: Ligand exchange, square planar, iridium, platinum

INTRODUCTION

Square planar complexes provide one of the foundations of coordination complexes. Substitutional reactivity of square planar complexes is dominated by associative reactions through trigonalbipyramidal intermediates/transition states.[1] However, Romeo has convincingly demonstrated that reactions of some platinum(II) square planar complexes occur by ligand loss to a three-coordinate complex.[2] In addition, two studies have shown the formation of $RhCl(PPh_3)_2$.[3,4] Triphenylphosphine dissociation from $RhCl(PPh_3)_3$ was found to occur with a rate constant of $0.71\ s^{-1}$.[3] Flash photolysis of $Rh(CO)(Cl)(PPh_3)_2$ also generated $RhCl(PPh_3)_2$ by CO dissociation.[4]

Sporadic reports of ligand exchange reactions *between* square planar complexes have appeared.[5-13] Garrow and Hartwell observed the exchange of halide, CO and phosphine ligands for iridium and rhodium complexes.[6] Halide and CO exchanges were suggested to occur through bridged intermediates; phosphine ligand

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* Author for correspondence.

exchange was ascribed to a dissociative process. Exchange of CO occurred in a minute, halide and phosphine exchange occurred in 3 minutes.[6] Strohmeier *et al.* had previously reported rapid exchange between trans-Ir(CO)(Cl)$(PPh_3)_2$ and trans-Ir(CO)(Cl)$(P(OPh)_3)_2$ but no exchange between trans-Ir(CO)(Cl)$(PCy_3)_2$ and trans-Ir(CO)(Cl)$(PPh_3)_2$ or trans-Ir(CO)(Cl)$(P(OPh)_3)_2$.[7] Sen and coworkers observed phosphine exchange between two palladium centers.[8] Reaction of Pd(C(O)Ph)Cl$(PPh_3)_2$ with Pd(C(O)Ph)Cl(P(p-tolyl)$_3)_2$ produced the mixed phosphine complex, Pd(C(O)Ph)Cl(PPh_3)(P(p-tolyl)$_3$). This phosphine scrambling reaction was attributed to phosphine dissociation.[8] Nelson and coworkers had also reported phosphine ligand exchange on palladium complexes.[9]

In addition to the Garrow and Hartwell studies of halide exchange involving square planar complexes, other reports have appeared. Puddephatt and Thompson reported the exchange of methyl and halogen groups on square planar platinum, gold and palladium complexes.[10] Stang and Huang have recently reported the exchange of the triflate group of M(CO)(OTf)$(PPh_3)_2$, M = Rh, Ir, with a number of complexes.[11] The triflate exchanged with Cl^- in reactions between square planar complexes.[11] Double exchange of two chlorides between a square planar complex and an octahedral dihalide complex was reported.[12] In this case a double chloride-bridged intermediate was suggested.[12]

We have previously communicated phosphine ligand exchange between iridium(I) centers.[13] In this manuscript we show that such exchange reactions occur between Ir(I) centers, Ir(I) and Pt(II) centers, and between Pt(II) centers. These results indicate a reaction initiated by phosphine dissociation from the iridium center.

EXPERIMENTAL

All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Mattson Polaris Fourier-transform infrared spectrophotometer. ^1H and ^{31}P spectra were recorded on a Varian VXR-400 spectrometer using d^8-toluene, $CDCl_3$, or CD_2Cl_2. The ^{31}P spectra reported are proton decoupled and referenced to H_3PO_4.

The iridium complexes: trans-Ir(CO)(Cl)$(PPh_3)_2$, trans-Ir(CO)(Cl)(P(p-tolyl)$_3)_2$ and trans-Ir(CO)(Me)(P(p-tolyl)$_3)_2$,[14] and platinum complexes: cis-$PtCl_2(PPh_3)_2$, cis-$PtCl_2$(P(p-tolyl)$_3)_2$, cis-$PtCl_2(PMePh_2)_2$, trans-Pt(Cl)(H)$(PPh_3)_2$, trans-Pt(Cl)(H)$(PEt_3)_2$ and trans-Pt(Cl)(H)(P(p-tolyl)$_3)_2$ were prepared according to literature procedures.[15] A mixture of cis- and trans-$PtCl_2(PEt_3)_2$ was prepared according to literature procedures.[16] The mixture was cleanly separated by extraction of the trans isomer into ether.[16b] The spectral characterizations were consistent with those previously reported. The ^{31}P resonances are collected in Table 1. These observed resonances are consistent with those previously reported.[14–16] All platinum compounds show the satellites expected from Pt-P coupling.

Reactions at room temperature were accomplished by two methods:

(*A*) Reaction of an iridium complex with a platinum complex is illustrated for reaction of trans-Ir(CO)(Me)(P(p-tolyl)$_3)_2$ with trans-Pt(Cl)(H)$(PPh_3)_2$. In an NMR tube equipped with a vacuum adapter 0.011 g (1.3×10^{-5} mol) of trans-Ir(CO)(Me)(P(p-tolyl)$_3)_2$ and 0.010 g (1.3×10^{-5} mol) of Pt(Cl)(H)$(PPh_3)_2$ are dissolved in 1 ml of d^8 toluene. This tube is removed from the inert atmosphere glove box and sealed on a high-vacuum line. Reaction progress is monitored by ^{31}P NMR.

Table 1 Observed ^{31}P resonances for phosphine ligands in square planar complexes.

Complex	CD_2Cl_2	$CDCl_3$	d^8-toluene
P(p-tolyl)$_3$	-7.96(s)		
PPh$_3$	-5.25(s)		
PMePh$_2$	-26.85(s)		
trans-Ir(CO)(Cl)(PMePh$_2$)$_2$	9.4(s)		
trans-Ir(CO)(Me)(PMePh$_2$)$_2$	10.2(s)		
trans-Ir(CO)(OMe)(PMePh$_2$)$_2$	13.8(s)		
trans-Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$	22.5(s)	24.0(s)	22.9(s)
trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$	28.2(s)		29.6(s)
trans-Ir(CO)(Cl)(PMePh$_2$)(P(p-tolyl)$_3$)	10.1(d), 29.0(d)		
trans-Ir(CO)(Me)(PMePh$_2$)P(p-tolyl)$_3$)	9.9(d), 23.0(d)		
trans-Ir(CO)(OMe)(PMePh$_2$)(P(p-tolyl)$_3$)	13.5(d), 25.6(d)		
trans-Ir(CO)(Cl)(PPh$_3$)$_2$		25.5(s)	23.6(s)
trans-Ir(CO)(Cl)(PPh$_3$)(P(p-tolyl)$_3$)		24.6(s), 25.3(s)	22.2(s), 22.9(s)
trans-Ir(CO)(Me)(PPh$_3$)$_2$	32.5(s)		31.8(s)
trans-Ir(CO)(Me)(PPh$_3$)(P(p-tolyl)$_3$)	32.3(d), 30.0(d)*		32.3(d), 30.0(d)*
trans-Ir(CO)(Cl)(PEt$_3$)$_2$		21.4(s)	20.2(s)
trans-Ir(CO)(Cl)(PEt$_3$)(PPh$_3$)		21.1(d), 27.5(d)*	
cis-PtCl$_2$(P(p-tolyl)$_3$)$_2$		14.4(s)	
cis-PtCl$_2$(PPh$_3$)$_2$	14.5(s)	16.2(s)	
cis-PtCl$_2$(PPh$_3$)(P(p-tolyl)$_3$)	16.2(d), 13.7(d)	16.5(d), 14.1(d)	
trans-Pt(Cl)(H)(PEt$_3$)$_2$		24.8(s)	23.4(s)
trans-Pt(Cl)(H)(PPh$_3$)$_2$			28.8(d)
trans-Pt(Cl)(H)(PEt$_3$)(PPh$_3$)		25.3(d), 31.1(d)*	
trans-Pt(Cl)(H)(P(p-tolyl)$_3$)$_2$			26.6(d)
trans-Pt(Cl)(H)(PPh$_3$)(P(p-tolyl)$_3$)			28.2(d), 27.5(d)
cis-PtCl$_2$(P(p-C$_6$H$_4$OMe)$_3$)$_2$	10.8(s)		
trans-PtCl$_2$(PEt$_3$)$_2$		14.1(s)	
cis-PtCl$_2$(PEt$_3$)(PPh$_3$)		14.8(d), 7.3(d)	
cis-PtCl$_2$(PEt$_3$)(P(p-tolyl)$_3$)		12.8(d), 7.1(d)	
cis-PtCl$_2$(PEt$_3$)$_2$		10.9(s)	

* Second order spectrum.

(*B*) Reaction of two platinum complexes are described for reaction of $PtCl_2(PPh_3)_2$ with $PtCl_2(P(p\text{-tolyl})_3)_2$. In a 3 dram vial 0.020 g (2.5×10^{-5} mol) of $PtCl_2(PPh_3)_2$ and 0.022 g (2.5×10^{-5} mol) of $PtCl_2(P(p\text{-tolyl})_3)_2$ are dissolved in 3 ml of $CDCl_3$ in an inert atmosphere glove box. A one ml aliquot of the mixture is put in an NMR tube. Reaction progress is monitored by ^{31}P NMR.

Reaction of two iridium complexes occurs rapidly even at low temperature. In a typical reaction, 25 mg of trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ and 25 mg of trans-Ir(CO)(Cl)(PMePh$_2$)$_2$ were placed in an NMR tube equipped with a vacuum adaptor, which was then removed from the inert-atmosphere glove box and placed on a high-vacuum line. The solids were evacuated and cooled to N_2(l) temperature, and 1.0 ml of CD_2Cl_2 was added by vacuum distillation. The sample was placed frozen in the NMR instrument and monitored from $-70°C$ to room temperature by ^{31}P NMR spectroscopy.

Half-life estimates were accomplished through integration of the ^{31}P spectra for room temperature reactions. Since we have not established a first order rate law, these should be considered as measures of reaction progress. The time selected was when the reaction had proceeded halfway to the equilibrium mixture. Error limits on the half-lives should be considered as ±10%.

RESULTS

The reactions reported in this manuscript involve the exchange of phosphine ligands between square planar complexes of iridium and platinum. Results for each reaction type will be described separately.

Iridium(I)-Iridium(I)

Phosphine exchange between iridium(I) complexes occurs readily resulting in the mixed phosphine complex.[17]

$$\begin{aligned} &\mathrm{Ir(CO)(X)L_2 + Ir(CO)(X')L'_2 \rightleftarrows Ir(CO)(X)LL'} \\ &\quad \mathrm{+\ Ir(CO)(X)L'_2 + Ir(CO)(X')LL' + Ir(CO)(X')L_2} \qquad (1) \\ &\mathrm{X,X' = Cl, OMe, Me} \\ &\mathrm{L = P(p\text{-}tolyl)_3, PPh_3, PMePh_2} \end{aligned}$$

The ^{31}P spectrum for such a reaction is shown in Figure 1 for reaction of trans-$Ir(CO)(Me)(P(p\text{-}tolyl)_3)_2$ with trans-$Ir(CO)(Cl)(PMePh_2)_2$. The two reactants and four products are clearly seen in the ^{31}P spectrum. These exchange reactions are quite rapid, even occurring at −70°C. The equilibrium mixture contains statistical amounts of each product. For the iridium products the coupling of the trans-phosphine ligands is observed in the mixed phosphine complexes only when $PMePh_2$ is used in CD_2Cl_2 or for the 2nd order spectra observed for PEt_3 complexes.

Iridium(I)-Platinum(II)

Reaction of trans-$Ir(CO)(Cl)(PPh_3)_2$ with cis-$Pt(Cl)_2(P(p\text{-}tolyl)_3)_2$ results in formation of the mixed species.

$$\begin{aligned} &\mathrm{trans\text{-}Ir(CO)(Cl)(PPh_3)_2 + cis\text{-}PtCl_2(P(p\text{-}tolyl)_3)_2 \rightleftarrows} \\ &\quad \mathrm{trans\text{-}Ir(CO)(Cl)(PPh_3)(P(p\text{-}tolyl)_3) + trans\text{-}Ir(CO)(Cl)(P(p\text{-}tolyl)_3)_2} \qquad (2) \\ &\quad \mathrm{+\ cis\text{-}PtCl_2(PPh_3)(P(p\text{-}tolyl)_3) + cis\text{-}PtCl_2(PPh_3)_2} \end{aligned}$$

This phosphine exchange reaction takes place with a half-life of hours at ambient conditions. Phosphorus coupling is seen for the mixed phosphine platinum product ($J_{P-P} = 15.7$ Hz consistent with a cis geometry) but is not seen for the iridium mixed phosphine complex. The spectrum is shown in Figure 2. A similar reaction occurs for trans-$Ir(CO)(Cl)(PPh_3)_2$ and trans-$PtCl_2(PEt_3)_2$ with a half-life of 12 h. For $Ir(CO)(Cl)(PEt_3)(PPh_3)$ a second order spectrum is observed (the ^{31}P data are shown in Table 1).

Reaction of trans-$Ir(CO)(Me)(P(p\text{-}tolyl)_3)_2$ with trans-$Pt(Cl)(H)L_2$ ($L = PPh_3$ and PEt_3) also leads to exchange.

$$\begin{array}{ccc} & & \mathrm{trans\text{-}Ir(CO)(Me)L_2} \\ & & + \\ \mathrm{trans\text{-}Ir(CO)(Me)(P(p\text{-}tolyl)_3)_2} & & \mathrm{trans\text{-}Ir(CO)(Me)L(P(p\text{-}tolyl)_3)} \\ + & \rightleftarrows & + \\ \mathrm{trans\text{-}Pt(Cl)(H)L_2} & & \mathrm{trans\text{-}Pt(Cl)(H)(P(p\text{-}tolyl)_3)_2} \\ & & + \\ & & \mathrm{trans\text{-}Pt(Cl)(H)L(P(p\text{-}tolyl)_3} \end{array} \qquad (3)$$

$$\mathrm{L = PPh_3, PEt_3}$$

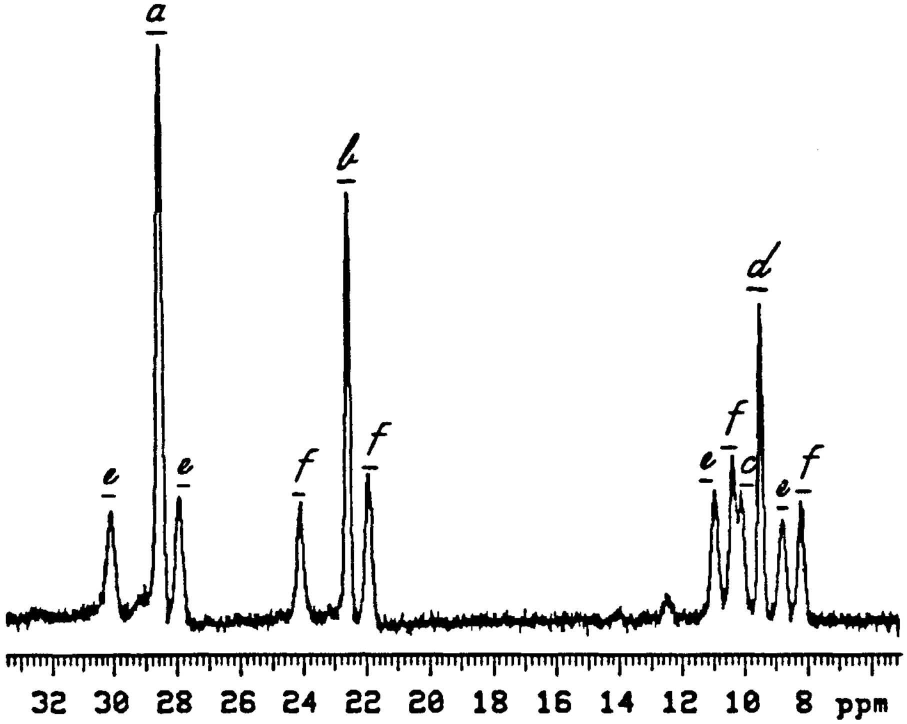

Figure 1 ^{31}P NMR spectrum of the product mixture for reaction of trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ with trans-Ir(CO)(Cl)(PMePh$_2$)$_2$. The resonance labeled *a* corresponds to trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$, *b* to trans-Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$, *c* to trans-Ir(CO)(Me(PMePh$_2$)$_2$, *d* to trans-Ir(CO)(Cl)(PMePh$_2$)$_2$, the resonances labeled *e* correspond to trans-Ir(CO)(Me)(P(p-tolyl)$_3$)(PMePh$_2$) and *f* to trans-Ir(CO)(Cl)(P(p-tolyl)$_3$)(PMePh$_2$).

The ^{31}P spectrum is shown in Figure 3. The four downfield resonances are assigned to trans-Ir(CO)(Me)(PPh$_3$)$_2$ at 31.9 ppm, trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ at 29.8 ppm and trans-Ir(CO)(Me)(P(p-tolyl)$_3$)(PPh$_3$) at 31.4 and 30.3 ppm. The resonances between 26 and 29 ppm arise from the platinum bound phosphines. Each of these is a doublet from coupling to the hydride (J_{P-H} = 9.7 Hz). Platinum coupling ($J_{Pt-P} \cong 3000$ Hz) is observed for these resonances. The remaining ^{31}P resonances correspond to the phosphines on Ir(CO)(Cl)L$_2$ formed later in the reaction. Note that the chemical shifts are shifted 2 ppm for d^8 toluene in comparison to CDCl$_3$. The ^1H NMR spectrum shows the effect of the ligand scrambling in the resonance of the methyl. The triplet observed for the starting complex becomes a seven line spectrum corresponding to the overlap of three triplets with nearly identical coupling constants. The 1:2:3:4:3:2:1 resonance shown in Figure 4 is as expected for a statistical distribution of the three products.

Reaction of trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ with cis-PtCl$_2$(PPh$_3$)$_2$ also leads to exchange.

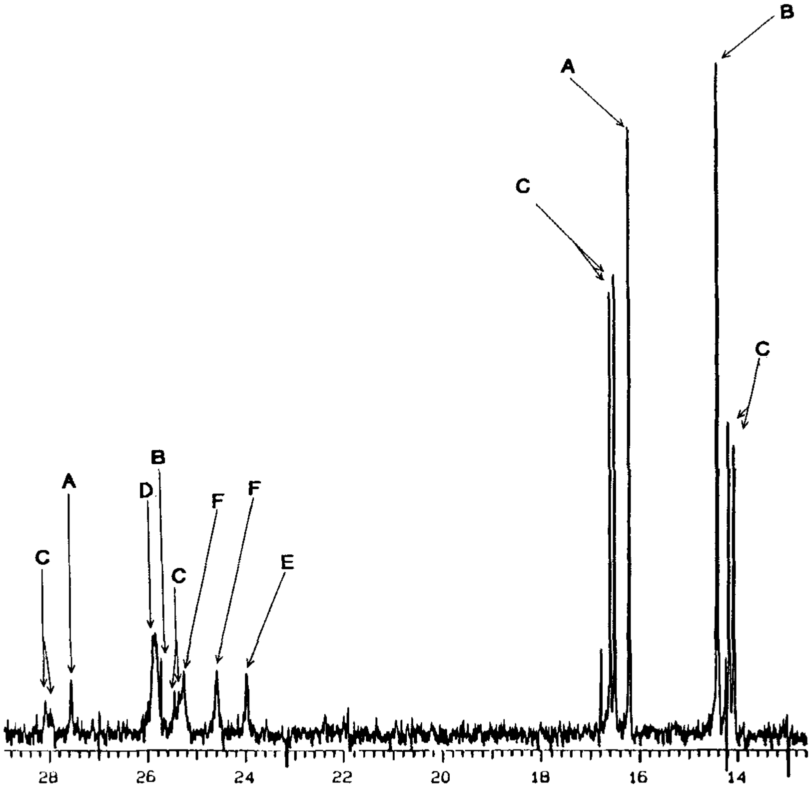

Figure 2 The ^{31}P spectrum for the reaction products from reaction of cis-PtCl$_2$(PPh$_3$)$_2$ with trans-Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$. The following labels indicate the products: *a* cis-PtCl$_2$(PPh$_3$)$_2$, *b* cis-PtCl$_2$(P(p-tolyl)$_3$)$_2$, *c* cis-PtCl$_2$(PPh$_3$)(P(p-tolyl)$_3$), *d* Ir(CO)(Cl)(PPh$_3$)$_2$, *e* Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$ and *f* Ir(CO)(Cl)(PPh$_3$)(P(p-tolyl)$_3$).

$$\begin{array}{ccc} & & \text{trans-Ir(CO)(Me)(P(p-tolyl)}_3\text{)(PPh}_3\text{)} \\ & & + \\ \text{trans-Ir(CO)(Me)(P(p-tolyl)}_3\text{)}_2 & & \text{trans-Ir(CO)(Me)(PPh}_3\text{)}_2 \\ + & \rightleftarrows & + \\ \text{cis-PtCl}_2\text{(PPh}_3\text{)}_2 & & \text{cis-PtCl}_2\text{(P(p-tolyl)}_3\text{)(PPh}_3\text{)} \\ & & + \\ & & \text{cis-PtCl}_2\text{(P(p-tolyl)}_3\text{)}_2 \end{array} \qquad (4)$$

All species are identified by ^{31}P NMR. Resonances are listed in Table 1. The methyl protons on iridium are observed as a triplet (J_{H-P} = 9 Hz) for the reactant; the methyl protons of the iridium products grow underneath the original triplet over time. Reaction half-life is three days. No exchange is observed between trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ and cis-PtCl$_2$(PEt$_3$)$_2$ over seven days. Methyl transfer is not observed for either reaction.

Phosphine ligand exchange is also observed for reaction of trans-Ir(CO)(Cl)(PPh$_3$)$_2$ with trans-Pt(Cl)(H)(PEt$_3$)$_2$. The mixed phosphine products,

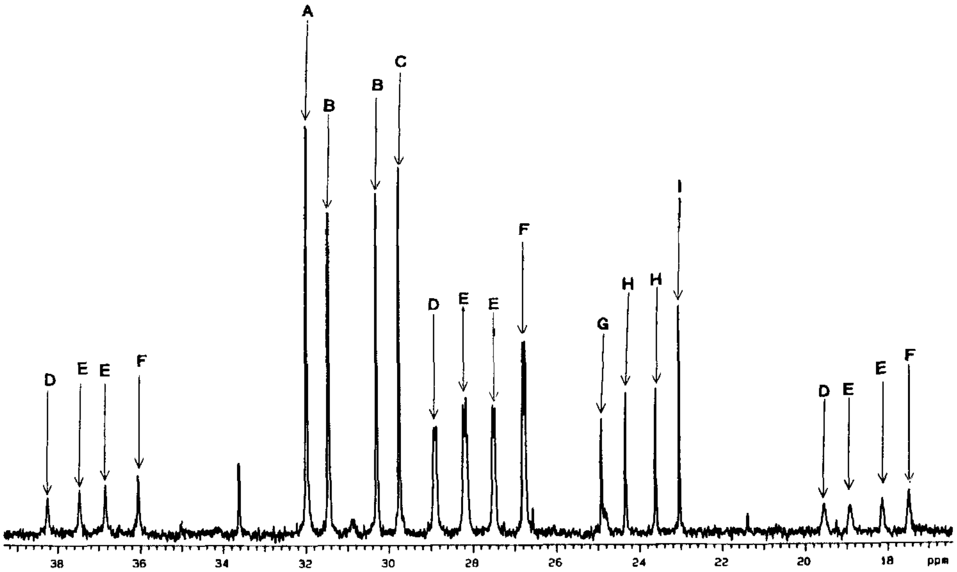

Figure 3 The observed ^{31}P spectrum for reaction of trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ with trans-Pt(Cl)(H)(PPh$_3$)$_2$. The resonances centered around 31 are from iridium methyl compounds; those around 28 are from platinum hydrido complexes; those at 24 from iridium chloro complexes; and those at 37 and 19 are satellites from platinum coupling in the hydrido chloro compound. The detailed assignments follow: *a* trans-Ir(CO)(Me)(PPh$_3$)$_2$, *b* trans-Ir(CO)(Me)(PPh$_3$)(P(p-tolyl)$_3$), *c* trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$, *d* trans-Pt(H)Cl(PPh$_3$)$_2$, *e* trans-Pt(H)Cl(PPh$_3$)(P(p-tolyl)$_3$), *f* trans-Pt(H)Cl(P(p-tolyl)$_3$)$_2$, *g* trans-Ir(CO)(Cl)(PPh$_3$)$_2$, *h* trans-Ir(CO)(Cl)(PPh$_3$)(P(p-tolyl)$_3$), and *i* trans-Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$.

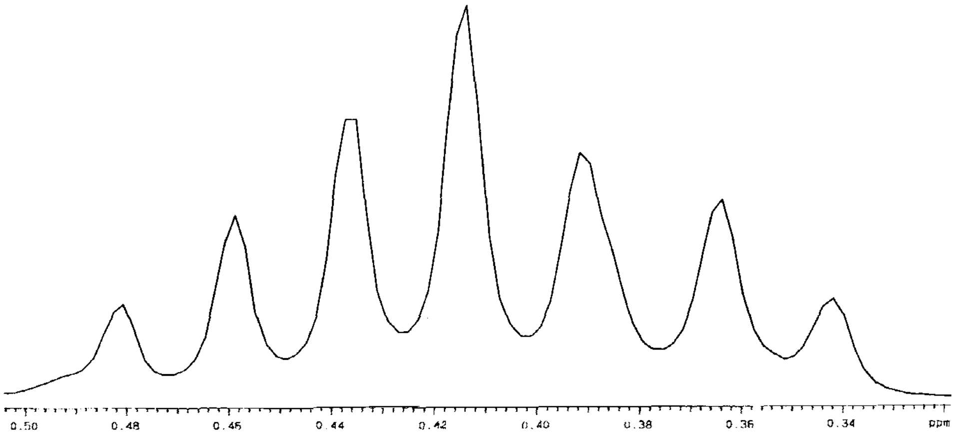

Figure 4 The methyl region of the ^1H NMR spectrum for reaction of trans-Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$ with trans-Pt(Cl)(H)(PPh$_3$)$_2$. The resonance is composed of overlapping triplets of a 1:2:1 ratio of the three iridium methyl complexes (Ir(CO)(Me)(PPh$_3$)$_2$, Ir(CO)(Me)(PPh$_3$)(P(p-tolyl)$_3$) and Ir(CO)(Me)(P(p-tolyl)$_3$)$_2$.

$trans$-Pt(Cl)(H)(PEt_3)(PPh_3) and $trans$-Ir(CO)(Cl)(PEt_3)(PPh_3), both exhibit 2nd order ^{31}P spectra. Analysis leads to $\nu(PPh_3) = 31.1$ ppm, $\nu(PEt_3) = 25.3$ ppm with $J(P\text{-}P) = 407$ Hz for the mixed phosphine platinum complex and $\nu(PPh_3) = 27.5$ ppm, $\nu(PEt_3) = 21.1$ ppm with $J(P\text{-}P) = 336$ Hz for the mixed phosphine iridium complex.

Platinum(II)-Platinum(II)

Reaction of trans-Pt(Cl)(H)(P(p-tolyl)$_3$)$_2$ with trans-Pt(Cl)(H)L_2, $L = PPh_3$ and PEt_3, gives the phosphine ligand exchange product.

$$\begin{array}{l} \text{trans-Pt(Cl)(H)(P(p-tolyl)}_3)_2 \\ \quad + \\ \text{trans-Pt(Cl)(H)(L)}_2 \\ L = PPh_3 \text{ and } PEt_3 \end{array} \rightleftarrows 2\ \text{trans-Pt(Cl)(H)(P(p-tolyl)}_3)\text{L} \qquad (5)$$

For these reactions the ^{31}P spectra are identical to the portion of the spectra attributed to platinum products in reaction with methyl iridium complexes. The ^1H spectrum for $L = PPh_3$ shows only a multiplet centered at -15.3 ppm. However, for $L = PEt_3$, the three hydride products and their coupling to platinum are clearly shown (Figure 5). The phosphine ligands have statistically scrambled as for the other exchanges.

Reactions between Pt(II) dichlorides also lead to exchange products.

$$\text{cis-}PtCl_2L_2 + \text{cis-}PtCl_2L'_2 \rightleftarrows 2\ \text{cis-}PtCl_2LL' \qquad (6)$$

$L, L' = PPh_3$, P(p-tolyl)$_3$ and PEt_3

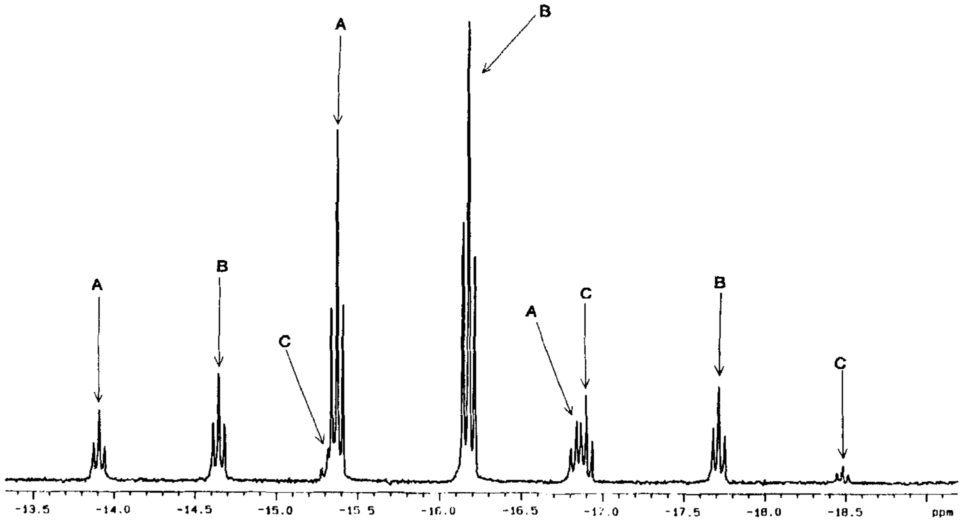

Figure 5 The hydride portion of the ^1H NMR spectrum for exchange reactions of trans-Pt(Cl)(H)(P(p-tolyl)$_3$)$_2$ and trans-Pt(Cl)(H)(PEt_3)$_2$. The coupling of the hydride to phosphorus and platinum is clearly shown. The assignments are: *a* trans-Pt(Cl)(H)(P(p-tolyl)$_3$)$_2$, *b* trans-Pt(Cl)(H)(P(p-tolyl)$_3$)(PEt_3), and *c* trans-Pt(Cl)(H)(PEt_3)$_2$.

These exchange reactions are relatively slow with half-lives of hours. The reaction rate depends on the nature of the phosphine ligand. For $L = PPh_3$ and $L' = P(p\text{-tolyl})_3$ the reaction has a half-life of ~3 hours; for $L = PEt_3$ and $L' = P(p\text{-tolyl})_3$ the reaction half-life is 40 hours. For PEt_3 as a ligand, reaction of the trans isomer has also been examined. The exchange reaction

$$\text{trans-}PtCl_2(PEt_3)_2 + \text{cis-}PtCl_2(P(p\text{-tolyl})_3)_2 \rightleftarrows \text{exchange} \quad (7)$$

occurs with a half-life of ~12 hours. This reaction produces the mixed phosphine product, $PtCl_2(PEt_3)(P(p\text{-tolyl})_3)$ that is identical to that produced from the analogous reaction of cis-$PtCl_2(PEt_3)_2$. Based on the $J_{P-P} = 16.2$ Hz we believe that the cis isomer is formed. In the reaction of cis-$PtCl_2(PEt_3)_2$ a small amount of trans-$PtCl_2(PEt_3)_2$ is formed. Interestingly, in the similar reaction of trans-$PtCl_2(PEt_3)_2$, cis-$PtCl_2(PEt_3)_2$ is a product. Thus, the phosphine ligand exchange is accompanied by an isomerization. The cis isomer is favored (4:1) over the trans isomer.

DISCUSSION

The reactions under consideration involve scrambling of phosphine ligands between metal centers of square planar complexes. The current examples, coupled with previous observations,[5-13] indicate that this is a general, though not widely recognized, reaction of square planar complexes. Exchange has now been observed between: (1) two palladium centers,[8,9] (2) two rhodium centers,[6] (3) two iridium centers,[7,13] (4) rhodium and iridium centers,[6] (5) iridium and platinum centers and (6) two platinum centers.

The primary technique for studying these exchange reactions is ^{31}P NMR which clearly shows the statistical distribution of the phosphine ligands. Two aspects of the ^{31}P NMR spectra for these bis-phosphine complexes need to be addressed: (1) Phosphorus-phosphorus coupling in the hetero-substituted complexes is observed for platinum centers (in addition to Pt-P coupling). This observed coupling is as expected for cis phosphine ligands ($J = \sim 20$ Hz). However, for the iridium complexes, $Ir(CO)(L)(L')X$, in this study, and the palladium and iridium complexes previously reported,[8,13] no P-P coupling is observed except for the 2nd order spectra observed for the iridium complexes containing PEt_3. This lack of coupling for trans phosphorus ligands has been discussed previously.[18] (2) Integration of the ^{31}P spectra usually show a statistical distribution of phosphine ligands in the complexes. However, for PEt_3 the NOE causes the integration to give an inaccurate representation of the amounts actually present.[19] Such effects have also been discussed previously.[6,20]

The relative rates, though not studied in detail, span quite a range. Those reactions involving metals other than platinum all occur quickly. The previous reports for Ir(I)-Ir(I), Ir(I)-Rh(I) and Pd(II)-Pd(II) exchanges show equilibrium established in under 5 minutes.[6,7,13] Indeed the phosphine exchanges reported herein between iridium centers reach equilibrium in minutes even at −70°C. The rapidity of these reactions precludes examination of metal center or ligand dependencies. Reactions that involve platinum centers are much slower, with half-lives of hours. The approximate half-lives for exchange are given in Table 2. Reactions between platinum complexes and complexes involving iridium occur

Table 2 Half-lives for the phosphine ligand exchange reactions.

$\text{trans-Ir(CO)Cl(PPh}_3)_2 + \text{cis-PtCl}_2(\text{P(p-tolyl)}_3)_2 \xrightarrow{t_{1/2}\,=\,7\text{h}}$

$\text{trans-Ir(CO)Cl(PPh}_3)_2 + \text{trans-PtClH(PEt}_3)_2 \xrightarrow{t_{1/2}\,=\,30\text{h}}$

$\text{trans-Ir(CO)Cl(PPh}_3)_2 + \text{trans-PtCl}_2(\text{PEt}_3)_2 \xrightarrow{t_{1/2}\,=\,12\text{h}}$

$\text{trans-Ir(CO)(Me)(P(p-tolyl)}_3)_2 + \text{cis-PtCl}_2(\text{PPh}_3)_2 \xrightarrow{t_{1/2}\,=\,3\text{d}}$

$\text{trans-Ir(CO)(Me)(P(p-tolyl)}_3)_2 + \text{cis-PtCl}_2(\text{PEt}_3)_2 \longrightarrow$ N.R. 7 days

$\text{cis-PtCl}_2(\text{PPh}_3)_2 + \text{trans-PtCl}_2(\text{PEt}_3)_2 \xrightarrow{t_{1/2}\,=\,60\text{h}}$

$\text{cis-PtCl}_2(\text{P(p-tolyl)}_3)_2 + \text{cis-PtCl}_2(\text{PEt}_3)_2 \xrightarrow{t_{1/2}\,=\,40\text{h}}$

$\text{cis-PtCl}_2(\text{P(p-tolyl)}_3)_2 + \text{trans-PtCl}_2(\text{PEt}_3)_2 \xrightarrow{t_{1/2}\,=\,12\text{h}}$

$\text{cis-PtCl}_2(\text{PPh}_3)_2 + \text{cis-PtCl}_2(\text{PEt}_3)_2 \longrightarrow$ N.R. 4 days

$\text{cis-PtCl}_2(\text{PPh}_3)_2 + \text{cis-PtCl}_2(\text{P(p-tolyl)}_3)_2 \xrightarrow{t_{1/2}\,=\,3\text{h}}$

$\text{trans-PtCl}_2(\text{PEt}_3)_2 + \text{PPh}_3 \longrightarrow$ cis in 45 minutes but not $\text{PtCl}_2(\text{PEt}_3)(\text{PPh}_3)$.
No change for next 2 days

$\text{cis-PtCl}_2(\text{PEt}_3)_2 + \text{PPh}_3 \longrightarrow$ trans in 30 min – reach same mix as with trans.

more rapidly than between analogous platinum complexes by about a factor or 2. A significant ligand effect is also present. The dichloroplatinum complexes illustrate the effect of phosphine ligands. Reaction of the PPh_3 complex with the P(p-tolyl)_3 complex occurs with a $t_{1/2} = 3\text{h}$; reaction of the P(p-tolyl)_3 complex with the cis-PEt_3 complex occurs with a $t_{1/2} = 40\text{h}$; and reaction of the PPh_3 complex with the cis-PEt_3 complex does not occur in 4 days. Thus the ligand effect for phosphine exchange is

$$\text{P(p-tolyl)}_3 > \text{PPh}_3 > \text{PEt}_3 \tag{8}$$

In addition, comparison of the dichloro complexes with the hydrido, chloro complex shows the dichloro to react faster by a factor of 2–3. The cis and trans isomers of $\text{PtCl}_2(\text{PEt}_3)_2$ allow the effect of geometry on phosphine ligand exchange to be assessed. In each case the trans isomer exchanges phosphine ligand more readily than the cis isomer.

The relative rate data are not of sufficient quality to warrant an extensive mechanistic discussion. However, the data reported in this manuscript are consistent with a phosphine dissociation mechanism as previously suggested.[5–13] There is precedence for ligand dissociation from square planar complexes.[2–4] Such a ligand dissociation could be consistent with the rhodium, iridium and palladium centers being more reactive than platinum since it would be expected that the Pt(II) center would bind L more strongly.

The relative rates for the iridium-iridium ligand exchange and iridium-platinum ligand exchange require that the rates of the associative ligand substitution be $k_{Ir} \geq 10^5 \times k_{Pt}$. Such substitutions from analogous Pt(II) and Ir(I) complexes apparently have not been reported, but it is known that iridium(I) centers undergo much more rapid ligand substitution than do Pt(II) centers.[1] Reaction of trans-$\text{Pt(PEt}_3)_2\text{Cl}_2$ with PPh_3 causes isomerization to cis-$\text{Pt(PEt}_3)_2\text{Cl}_2$, but does not give the mixed phosphine product, $\text{PtCl}_2(\text{PPh}_3)(\text{PEt}_3)$; however, the mixed product is formed from reaction of trans-$\text{PtCl}_2(\text{PEt}_3)_2$ with cis-$\text{PtCl}_2(\text{PPh}_3)_2$. To account for these observations with a phosphine dissociative process requires that the following reaction occur readily. The reaction of trans-$PtCl_2(PEt_3)_2$ with free PPh_3 would cause isomerization to

$$PtCl_2(PEt_3)_2 + PPh_3 \rightleftarrows PtCl_2(PEt_3)_2(PPh_3) \tag{9}$$

the mixture of cis- and trans-$PtCl_2(PEt_3)_2$ through the five-coordinate species, but the mixed square planar product would not be observed because of preferential binding of the strongly sigma bonding PEt_3 ligand. The five-coordinate intermediate is observed by ^{31}P NMR upon addition of PPh_3 to trans-$PtCl_2(PEt_3)_2$ as a doublet at 14.5 ppm and a triplet at 11.3 ppm with $J_{P-P} = 22$ Hz showing that PPh_3 coordinates. However, PPh_3 is not observed in any of the four-coordinate products.

A phosphine dissociative process would also be consistent with the lack of exchange reported between trans-$Ir(CO)(Cl)(PCy_3)_2$ and trans-$Ir(CO)(Cl)L_2$, L = PPh_3 or $P(OPh)_3$.[7] Since trans-$Ir(CO)(Cl)(PPh_3)_2$ and trans-$Ir(CO)(Cl)(P(OPh)_3)_2$ undergo exchange, dissociation from one of these complexes must occur. However, trans-$Ir(CO)(Cl)(PCy_3)_2$ is reported to be unreactive toward free PPh_3 and free $P(OPh)_3$.[7] Thus the lack of exchange between trans-$Ir(CO)(Cl)(PCy_3)_2$ and the other complexes is consistent with a dissociative process.

CONCLUSIONS

The reactions reported in this manuscript show that phosphine ligand exchange occurs readily between iridium and platinum centers. The relative rates for different phosphines ($P(p\text{-tolyl})_3 > PPh_3 > PEt_3$) and for the metal effect are best interpreted with an initial dissociation of a phosphine ligand from a square planar center.

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References

1. (a) F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions* (John Wiley: New York, 1968). (b) J.D. Atwood, *Inorganic and Organometallic Reaction Mechanisms* (Brooks/Cole: Monterey, CA, 1985).
2. (a) G. Alibrandi, L.M. Scolaro and R. Romeo, *Inorg. Chem.*, **30**, 4007 (1991). (b) R. Romeo, *Comments Inorg. Chem.*, **11**, 21 (1990). (c) G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, *J. Chem. Soc. A*, 1877 (1971).
3. J.A. Halpern and C.S. Wong, *J. Chem. Soc., Chem. Comm.*, 629 (1973).
4. D.A. Wink and P.C. Ford, *J. Am. Chem. Soc.*, **109**, 436 (1987).
5. P.E. Garrou, *Adv. Organomet. Chem.*, **23**, 95 (1984).
6. P.E. Garrou and G.E. Hartwell, *Inorg. Chem.*, **15**, 646 (1976).
7. W. Strohmeier, W. Rehder-Stirnweiss and G. Reischig, *J. Organomet. Chem.*, **17**, 393 (1971).
8. (a) J.S. Brumbaugh, R.R. Whittle, M. Parvez and A. Sen, *Organometallics*, **9**, 1735 (1990). (b) J.S. Brumbaugh and A. Sen, *J. Am. Chem. Soc.*, **110**, 803 (1988).
9. A.W. Verstuyft, D.A. Redfield, L.W. Cary and J.H. Nelson, *Inorg. Chem.*, **15**, 1128 (1976).

10. (a) R.J. Puddephatt and P.J. Thompson, *J. Organomet. Chem.*, **120**, C51 (1976). (b) R.J. Puddephatt and P.J. Thompson, *J. Chem. Soc. Dalton*, 1810 (1975).
11. P.J. Stang and Y.-H. Huang, *J. Organomet. Chem.*, **435**, 185 (1992).
12. S. Al-Jibori, C. Crocker and B.L. Shaw, *J. Chem. Soc. Dalton*, 319 (1981).
13. J.S. Thompson and J.D. Atwood, *J. Am. Chem. Soc.*, **113**, 7429 (1991).
14. (a) J.S. Thompson, K.A. Bernard, B.J. Rappoli and J.D. Atwood, *Organometallics*, **9**, 2727 (1990). (b) B.J. Rappoli, J.M. McFarland, J.S. Thompson and J.D. Atwood, *J. Coord. Chem.*, **21**, 147 (1990).
15. (a) G.W. Parshall, *Inorg. Synth.*, **12**, 26 (1974). (b) G.T. Kerr and A.E. Schweizer, *Inorg. Synth.*, **20**, 48 (1977).
16. (a) J. Chatt and R.G. Wilkins, *J. Chem. Soc.*, 2532 (1951). (b) J. Chatt and R.G. Wilkins, *J. Chem. Soc.*, 273 (1952).
17. The mixed phosphine products have not been previously reported. They are characterized only by ^{31}P NMR (Table 1). The resonances integrate as expected for statistical distribution and are identical for the mixed products formed from different reactants.
18. H.C. Clark, A.B. Goel and C.S. Wong, *J. Organomet. Chem.*, **190**, C101 (1980).
19. The PEt_3 ligand integrates consistently at ~3/2 of that expected.
20. J.H. Noggle and R.E. Schrier, *The Nuclear Overhauser Effect*, (Academic Press, New York, 1971).