Table I. Visible Absorption and Cyclic Voltammetric Data for Various Cis and Trans Complexes

$Ru(bpy)_2XY^{2+}$ XY	$E_{1/2}$,[a] V		λ_{max},[b] nm	
	cis	trans	cis	trans
$(py)_2$	1.30	1.28	455	475
$(pyz)_2$	1.18	1.11	473	480
$(CH_3CN)_2$	1.44	1.44	425	440
$(CH_3CN)(H_2O)$	[c]	1.15	445[d]	465
$(P(CH_3)_2(C_6H_5))_2$	1.45	1.33	396	431
$(P(CH_3)(C_6H_5)_2)_2$	1.52	1.39	387	427
$(H_2O)_2$	0.63[e]	0.46[e]	480	495

[a] $E_{1/2}$ vs. SSCE in CH_3CN/0.1 M TBAH. [b] Acetone solution except phosphines which are in acetonitrile and aquo complexes which are in 0.5 M CF_3COOH. [c] Rapid exchange of H_2O for solvent. [d] 1 N H_2SO_4. [e] 1 N aqueous CF_3COOH vs. SCE reference.

only one isomer is available, but some interesting trends are nevertheless apparent. The visible absorption maxima and $E_{1/2}$'s for all known cis-trans isomer pairs of ruthenium(II) complexes of the type $Ru(bpy)_2XY^{n+}$ are listed in Table I. The most obvious trend concerns the charge-transfer maxima. In every case the trans isomers absorb at lower energies than the corresponding cis isomers. These transitions have been assigned[16] as charge-transfer to ligand transitions, presumably to a π^* level of the bipyridine ligand. The Ru(III)/Ru(II) reduction potentials as reflected by the reversible $E_{1/2}$'s also show a consistent trend in that the trans isomers are oxidized at similar or less positive potentials than the corresponding cis isomers. Both of these observations suggest a stabilization of the $d\pi$ levels and a lowering of electron density at the Ru(II) center in the cis isomers relative to those in the trans isomers.[17]

Preliminary analysis of the infrared spectra of these complexes did not show any reliable differences which might be used to make a distinction between the two isomers.

A final word concerning the stability of the trans isomers is perhaps in order. Simply stated, they are remarkably stable and show little or no tendency to isomerize. Several attempts were made to quantify this aspect of the chemistry by measuring either kinetic or equilibrium parameters, but thermal isomerization could not be obtained in any of the complexes studied. The most extreme conditions employed consisted of heating acetone solutions of the complexes to 60 °C in sealed tubes for 12 h with 0.1 M ligand. No isomerization was observed with the trans complexes of pyridine, pyrazole, acetonitrile, or the substituted phosphines. The problem is under current consideration, and we are pursuing the possibility that the high ligand concentration is inhibiting the reaction, perhaps, by capturing one of the reaction intermediates before rearrangement can occur.

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Registry No. *trans*-$[Ru(bpy)_2(pyz)_2](PF_6)_2$, 79733-75-8; *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, 63358-69-0; *trans*-$[Ru(bpy)_2(CH_3CN)(H_2O)](ClO_4)_2$, 79681-78-0; *trans*-$[Ru(bpy)_2(CH_3CN)_2](ClO_4)_2$, 79732-91-5; *trans*-$Ru(bpy)_2Cl_2$, 34795-02-3; *trans*-$[Ru(Me_2bpy)_2(PPh_3)_2](PF_6)_2$, 79681-80-4; *trans*-$[Ru(Me_2bpy)_2(PPh_2Me)_2](PF_6)_2$, 79681-82-6; *trans*-$[Ru(Me_2bpy)_2(PPhMe_2)_2](PF_6)_2$, 79681-84-8; *trans*-$[Ru(bpy)_2(NO)(OH)](PF_6)_2$, 79681-86-0; *cis*-$[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$, 55124-54-4; *cis*-$[Ru(Me_2bpy)_2(PPh_3)(Cl)]PF_6$, 79681-88-2; *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$, 72203-26-0; $Ru(bpy)_2CO_3$, 59460-48-9; *cis*-$Ru(Me_2bpy)_2Cl_2$, 68510-55-4.

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Selectivity in Reactions of Alkyl-Aryl-Transition-Metal Complexes with Electrophiles

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The new methylarylmetal complexes *cis*-$[AuMe_2Ph(PPh_3)]$, *cis*-$[AuMe_2(4\text{-}MeC_6H_4)(PPh_3)]$, $[PtMe(4\text{-}MeC_6H_4)(C_8H_{12})]$, *cis*-$[PtMePh(PMePh_2)_2]$, and *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ have been prepared and characterized. In reactions with electrophilic reagents such as HCl, $HgCl_2$, and $[PtI_2(PMe_2Ph)_2]$, the complexes undergo selective cleavage of a methyl-metal bond (e.g., *cis*-$[PtMePh(PMePh_2)_2]$) or an aryl-metal bond (e.g., *cis*-$[AuMe_2Ph(PPh_3)]$, $[PtMe(4\text{-}MeC_6H_4)(C_8H_{12})]$). From the selectivity observed and from studies of relative rates of reaction, it is argued that the S_E2 mechanism leads to selective aryl-metal bond cleavage and that a different mechanism, probably involving an oxidative-addition-reductive-elimination sequence, leads to selective methyl-metal bond cleavage.

Introduction

There has been considerable interest in the mechanisms of reactions of electrophiles with alkyl and aryl derivatives of transition metals.[1] In such complexes there are typically high-energy occupied orbitals having M-C σ-bonding character and also nonbonding d orbitals.[1-4] Attack of the electrophile at a metal-carbon bond gives cleavage of this bond by the classical S_E2 mechanism,[5,6] but attack at the metal (oxidative addition) followed by reductive elimination can yield the same product.[1-4,7,8] This mechanism has been termed

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S_E(oxidative).[2] Mechanisms involving free radicals or electron-transfer mechanisms are also possible.[1,9] Differences between main-group metal alkyls and transition-metal alkyls are expected if the latter complexes use d orbitals in the initial interaction with the electrophile. One general feature which is observed in reactions of main-group compounds such as R_2Hg and R_4Sn with electrophiles is that aryl groups are cleaved very much more rapidly than alkyl groups.[5,6] For example, a phenyl group, R, is cleaved from $RSnMe_3$ 400–500 times as rapidly as a methyl group, R, and about 10^5 times as fast as an ethyl group in $RSnEt_3$ by mercury(II) halides.[10] In competition experiments, in compounds such as $PhSnMe_3$ or PhHgEt the phenyl group is always cleaved selectively by an electrophile. This behavior is easily understood since electrophilic aromatic substitution with a resonance stabilized "Wheland intermediate" is expected to occur more readily than electrophilic substitution at a saturated carbon.[1,5,6,10] The effect may be less pronounced in transition-metal derivatives. For example, a phenyl group, R, is cleaved from $[CoR(dmgh)_2(H_2O)]$ 7.4 times as fast as a methyl group, R, by Hg^{2+} in a reaction in which evidence for the S_E2 mechanism is strong (with inversion at carbon when R = alkyl).[11,12] Cleavage of the Fe–C bond in $[FeR(CO)_2(\eta^5\text{-}C_5H_5)]$ by mercury(II) halides is thought to occur by the S_E(oxidative) mechanism, and there is very little difference in reaction rate when R = methyl or phenyl.[2,3] In $[FePh(CO)_2(\eta^5\text{-}C_5H_5)]$ substitution in the phenyl ring para to iron may occur more rapidly than Fe–C bond cleavage.[13] In contrast to the above results, protonolysis of the first metal–carbon bond in *cis*-$[PtR_2(PEt_3)_2]$ occurs 10^6 times faster when R = Me than when R = Ph.[7] This remarkable difference was first attributed to the operation of an S_E(oxidative) mechanism, but it was later suggested that direct attack at a metal–carbon bond occurred in both cases.[14,15]

One problem in interpreting results based on rate constants is that by changing the alkyl or aryl groups the steric effects in the organometallic complex are also changed, and these may be at least partly responsible for the rate differences. For this reason, we undertook a study of the selectivity of cleavage of alkyl, R, or aryl, Ar, groups from transition-metal complexes of general formula $[MRArL_n]$, believing that this would provide new mechanistic insights. In this paper, the synthesis of alkylaryl derivatives of platinum and of gold is described together with some studies of cleavage reactions of the complexes. As far as we are aware, there have been no systematic studies of alkyl vs. aryl cleavage in transition-metal complexes, probably because the synthesis of the compounds is often difficult. A preliminary account has been published.[16]

Results and Discussion

Synthesis and Characterization. Our initial attempts to prepare complexes $[PtMePhL_2]$ in high purity were unsuccessful. Thus reaction of *cis*- or *trans*-$[PtClMe(PMe_2Ph)_2]$[17] or $[PtClMe(COD)]$[18] (COD = 1,5-cyclooctadiene) with phenyllithium gave considerable amounts of $[PtPh_2(PMe_2Ph)_2]$ or of $[PtPh_2(COD)]$. Similarly, reaction of *trans*-$[PtClPh(PMe_2Ph)_2]$ with methyllithium gave some *cis*-$[PtMe_2(PMe_2Ph)_2]$. Clearly phenyl for methyl exchange occurs as well as the desired phenyl or methyl for chloride exchange. A similar problem has been noted in related compounds.[19]

The above problem was avoided by using (nitrato)platinum(II) complexes.[20] The nitrate ligand is a very good leaving group and can be displaced easily without competing displacement of organic groups from platinum. The preferred synthetic methods are shown in Schemes I and II.

Scheme I

$$cis\text{-}[Pt(NO_3)_2(PMe_2Ph)_2] + [SnMe_3(4\text{-}MeC_6H_4)] \xrightarrow{-SnMe_3NO_3} trans\text{-}[Pt(NO_3)(4\text{-}MeC_6H_4)(PMe_2Ph)_2] \xrightarrow{MeLi,\ -LiNO_3} cis\text{-}[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$$

Scheme II

$$[PtI_2(COD)] + [SnMe_3(4\text{-}MeC_6H_4)] \xrightarrow{-SnMe_3I} [PtI(4\text{-}MeC_6H_4)(COD)] \xrightarrow[(ii)\ Me_4Sn,\ -SnMe_3NO_3]{(i)\ AgNO_3,\ -AgI} [PtMe(4\text{-}MeC_6H_4)(COD)]$$

In the case of the phosphine complexes (Scheme I) methyllithium was used as methylating agent in the final step since the milder tetramethyltin failed to react. The substitution occurred with a change of stereochemistry at platinum. The cis stereochemistry is expected to be most stable thermodynamically,[21] and it may be that stereochemical change occurs after the substitution of methyl for nitrate. However, in one synthesis, some *trans*-$[PtMePh(PMePh_2)_2]$ was also formed. For the cyclooctadiene case (Scheme II), our attempts to prepare pure alkyl(nitrato)- or aryl(nitrato)platinum(II) complexes were unsuccessful since they have low thermal stability. The complexes were therefore generated in situ by reaction of the corresponding iodide with silver nitrate, followed by immediate addition of tetramethyltin to give the desired product (Scheme II).

The desired *cis*-dimethylphenylgold(III) complexes were prepared without difficulty from the corresponding *cis*-dimethylchlorogold(III) complex, so that the use of nitrato intermediates was not necessary in this case (eq 1).[22]

$$cis\text{-}[AuMe_2Cl(PMe_3)] + PhMgBr \xrightarrow{-MgClBr} cis\text{-}[AuMe_2Ph(PMe_3)] \quad (1)$$

The characterization of the new compounds was straightforward, on the basis of the ^1H and ^{31}P NMR spectra. For example, *cis*-$[PtMePh(PMePh_2)_2]$ gave a methylplatinum resonance, appearing as four lines of equal intensity due to coupling to two nonequivalent ^{31}P atoms,[17] two methylphosphorus resonances, each appearing as a doublet, and two ^{31}P resonances, each showing a low coupling constant ^1J(PtP) typical of phosphorus atoms trans to carbon in platinum(II) complexes. The ^1J(PtP) values of 1873 and 1757 Hz can be compared with the analogous coupling of 1719 Hz in *cis*-

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Table I. Products of Reaction of Methyl(aryl)metal Complexes

complex	reagent	time[a]	products
cis-[$AuMe_2(4\text{-}MeC_6H_4)(PPh_3)$]	HCl	*b*	*cis*-[$AuClMe_2(PPh_3)$], PhMe
	$HgCl_2$	*b*	*cis*-[$AuClMe_2(PPh_3)$], [$HgCl(4\text{-}MeC_6H_4)$]
	[$PtI_2(PMe_2Ph)_2$]	2 days	*cis*-[$AuIMe_2(PPh_3)$], *trans*-[$PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
	[$PtCl_2(COD)$]		*cis*-[$AuClMe_2(PPh_3)$],[c] [$PtCl(4\text{-}MeC_6H_4)(COD)$]
	[$PtI_2(COD)$]	*b*	[$AuI(PPh_3)$], C_2H_6, [$PtI(4\text{-}MeC_6H_4)(COD)$]
cis-[$AuMe_2Ph(PPh_3)$]	HCl	*b*	*cis*-[$AuClMe_2(PPh_3)$], C_6H_6
cis-[$PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]	HCl	*b*	*cis*-[$PtCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$], CH_4
	$HgCl_2$	*b*	*cis*-[$PtCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$], [HgClMe]
	[$PtI_2(PMe_2Ph)_2$]	4 days	*trans*-[$PtIMe(PMe_2Ph)_2$], *trans*-[$PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
	[$PtI_2(PMePh_2)_2$]	3 days	*trans*-[$PtIMe(PMePh_2)_2$], *trans*-[$PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
	cis-[$PdCl_2(PMe_2Ph)_2$]	*b*	*trans*-[$PtCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$], *trans*-[$PdClMe(PMe_2Ph)_2$]
	[$AuCl(PMePh_2)$]	2 days	[$AuMe(PMePh_2)$],[d] *trans*-[$PtCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$][d]
	cis-[$AuClMe_2(PMePh_2)$]	6 h	[$AuMe_2(PMePh_2)$], *cis*-[$PtCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
cis-[$PtMePh(PMePh_2)_2$]	HCl	*b*	*cis*-[$PtClPh(PMePh_2)_2$], CH_4
[$PtMe(4\text{-}MeC_6H_4)(COD)$]	HCl	*b*	[$PtClMe(COD)$], PhMe
	$HgCl_2$	*b*	[$PtClMe(COD)$], [$HgCl(4\text{-}MeC_6H_4)$]
	[$PtI_2(PMe_2Ph)_2$]	30 days	[$PtIMe(COD)$], *trans*-[$PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
	cis-[$Pt(NO_3)_2(PMe_2Ph)_2$]	4 days	[$Pt(NO_3)Me(COD)$], *trans*-[$Pt(NO_3)(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]
	cis-[$PdCl_2(PMe_2Ph)_2$]	*b*	[$PtClMe(COD)$], *e*

[a] Approximate time to completion of reaction. [b] Less than 5 min. [c] Initially formed product, subsequently gives [$Au_2(\mu\text{-}Cl)_2Me_4$]. [d] This reaction is an equilibrium, and these products are in equilibrium with starting materials. [e] The product is presumed to be [$PdCl(4\text{-}MeC_6H_4)(PMe_2Ph)_2$], but the product decomposed.

[$PtMe_2(PEt_3)_2$].[24,25] In addition the low value of $^2J(PP)$ of 12 Hz is typical for cis phosphines whereas values of 550–830 Hz are seen for trans phosphines.[24,25] *cis*-[$AuMe_2(4\text{-}MeC_6H_4)(PPh_3)$] gave three methyl resonances of equal intensity. Two of these were doublets at 0.13 ppm, $^3J(PH)$ = 6.6 Hz, and 1.07 ppm, $^3J(PH)$ = 9.6 Hz, assigned as due to methylgold groups trans to aryl- and triphenylphosphine, respectively, and the other was a singlet at 2.13 ppm due to the tolyl group. These data define the cis stereochemistry unambiguously.[23,26] Complete NMR data is given in the Experimental Section.

Reactions with Electrophiles. Some results of the cleavage reactions are given in Table I. The reagents were mixed in a 1:1 mole ratio, and the reactions were then usually monitored with NMR spectroscopy. In this way, the rate of reaction and nature of products could be determined. Whenever possible, the products were isolated and fully characterized, but, when the electrophile was a transition-metal complex, this was not possible and products were identified by their NMR spectra. In all cases, the pure products were synthesized by alternative routes so that direct comparison with NMR spectra of authentic compounds was possible. With the choice of complexes with rich NMR spectra, positive identification was achieved in almost all cases. The only problems encountered were in reactions of *cis*-[$AuMe_2(4\text{-}MeC_6H_4)(PPh_3)$] with transition-metal halides when the initially formed *cis*-[$AuXMe_2(PPh_3)$] underwent dissociation of phosphine or reductive elimination of ethane in some cases. These reactions are not unexpected and have been investigated previously.[27,28] The selectivity of the initial cleavage reaction is not affected by these secondary reactions.

It is shown that the selectivity of cleavage of a methyl or an aryl group is not affected by the choice of electrophilic reagent since electrophiles as different as HCl or [$PtI_2(PMe_2Ph)_2$] give the same selectivity (Table I). However, there is a dramatic dependence on the nature of the methylarylmetal derivative. All electrophiles studied cleave an aryl group from *cis*-[$AuMe_2(4\text{-}MeC_6H_4)(PPh_3)$], *cis*-[$AuMe_2Ph(PPh_3)$], and [$PtMe(4\text{-}MeC_6H_4)(COD)$] but a methyl group was cleaved selectively from *cis*-[$PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2$] and *cis*-[$PtMePh(PMePh_2)_2$]. In all cases, the degree of selectivity was at least 90% and in most cases at least 95%, as evidenced by the absence of peaks due to the alternative products in the NMR spectra of reaction mixtures.

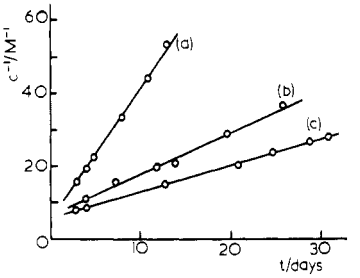

Figure 1. Second-order plots for the reaction of [$PtI_2(PMe_2Ph)_2$] with (a) [$PtMe(4\text{-}MeC_6H_4)(COD)$], (b) [$Pt(4\text{-}MeC_6H_4)_2(COD)$], and (c) [$PtMe_2(COD)$]. In each case the disappearance of the COD complex (concentration *c*, initial concentration 0.2 M) was monitored.

Table II. Rates of Reaction of the Complexes with [$PtI_2(PMe_2Ph)_2$] at 25 °C

complex	approx react time, days	10^5k_2, L mol^{-1} s^{-1}
[$AuMe_3(PMe_2Ph)$]	1	60[a]
cis-[$AuMe_2(4\text{-}MeC_6H_4)(PMe_2Ph)$]	2	32[a]
cis-[$PtMe_2(PMe_2Ph)_2$]	1	70[a]
cis-[$PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2$]	4	20[a]
trans-[$Pt(4\text{-}MeC_6H_4)_2(PMe_2Ph)_2$]	*c*	$\ll 1$[a]
[$PtMe_2(COD)$]	60	0.8[b]
[$PtMe(4\text{-}MeC_6H_4)(COD)$]	30	4.2[b]
[$Pt(4\text{-}MeC_6H_4)_2(COD)$]	35	1.5[b]

[a] Solvent CH_2Cl_2. [b] Solvent $CDCl_3$. [c] Very slow at 25 °C; complete in ca. 2 weeks at 60 °C.

Approximate kinetic data was obtained for reactions with [$PtI_2(PMe_2Ph)_2$] and the results are shown in Figure 1 and Table II. The reactions were carried out using equimolar and standard concentrations of [$PtI_2(PMe_2Ph)_2$] and the alkyl or arylmetal derivative in sealed NMR tubes. The reactions followed overall second-order kinetics, presumably first order with respect to each reagent, but this has not been checked.[20,29]

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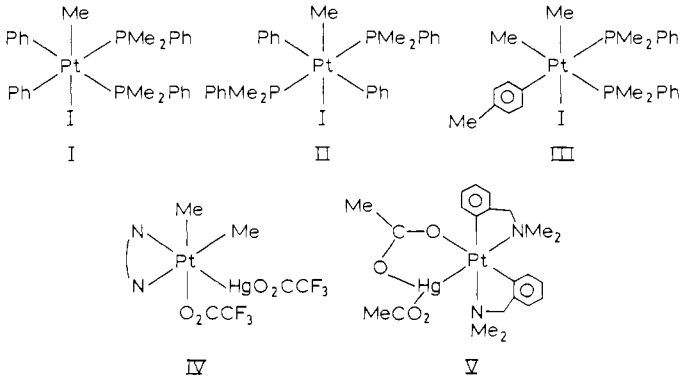
The aim was just to compare relative reactivities rather than to obtain accurate rate constants. The rates follow the sequences *cis*-$[PtMe_2(PMe_2Ph)_2]$ > *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ >> *trans*-$[Pt(4\text{-}MeC_6H_4)_2(PMe_2Ph)_2]$, $[PtMe(4\text{-}MeC_6H_4)(COD)]$ > $[Pt(4\text{-}MeC_6H_4)_2(COD)]$ > $[PtMe_2(COD)]$, and $[AuMe_3(PMe_2Ph)]$ > *cis*-$[AuMe_2(4\text{-}MeC_6H_4)(PMe_2Ph)]$. It can be seen that the range of reaction rates for cleavage of [PtRR′(COD)] where R, R′ = Me, $4\text{-}MeC_6H_4$ is small with only a factor of 2 between $[PtMe_2(COD)]$ and $[Pt(4\text{-}MeC_6H_4)_2(COD)]$ (the aryl derivative reacts faster). However, there is a very much greater difference in reactivity between the rates for *cis*-$[PtMe_2(PMe_2Ph)_2]$ and *trans*-$[Pt(4\text{-}MeC_6H_4)_2(PMe_2Ph)_2]$, with the methyl derivative reacting much faster.

Discussion. When this work began, we believed that it should be possible to distinguish between the classical S_E2 mechanism of electrophilic cleavage of metal–carbon bonds and a mechanism based on an oxidative-addition–reductive-elimination sequence by study of the selectivity of alkyl vs. aryl cleavage.[16] The precedents for believing that the S_E2 mechanism would lead to selective cleavage of an aryl group are given in the Introduction. What is the evidence for believing that the S_E(oxidative) mechanism should lead to selective cleavage of a methyl group? Since reductive elimination is likely to be a concerted process in the reactions of interest, bond strength considerations may well be dominant with weaker M–C bonds cleaved more readily. The mean Pt–C bond dissociation energy in $[PtPh_2(PEt_3)_2]$ is thought to be 250 kJ mol^{-1}, but in *fac*-$[PtIMe_3(PMe_2Ph)_2]$ it is 144 kJ mol^{-1} and, although both values are obtained with indirect methods, it seems likely that the phenyl–platinum bond is stronger than the methyl-platinum bond.[30,31] In reductive eliminations from platinum(IV) there is also direct evidence that methyl groups are eliminated more easily than phenyl groups. Thus Clark showed that $[PtIMePh_2(PMe_2Ph)_2]$, as a mixture of isomers I and II decomposed to give toluene and *trans*-$[PtIPh(PMe_2Ph)_2]$. We have shown that methyl iodide reacted with *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ to give $[PtIMe_2(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ (III), which then decomposed to ethane and *trans*-$[PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ by selective elimination of methyl groups. For concerted reductive elimination to occur, the groups to be eliminated must be mutually cis and this is certainly a complicating factor; for example, II cannot undergo elimination of biphenyl without prior isomerization. Such isomerization is normally faster than reductive elimination, as in the above case, but this cannot be assumed unless the isomerization can be studied separately.[31,32]



I II III IV V

The above situation applies to platinum(IV) but may not apply to transition-metal complexes generally. Halpern has shown that the rate of reductive elimination from $[PtHR(PPh_3)_2]$ is greater for R = Ph than for R = Me.[33] This could be a steric effect. Thus reductive elimination from I to III is faster than from $[PtIMe_3(PMe_2Ph)_2]$ yet the methyl groups are eliminated selectively. However, we found that *cis*-$[AuMe_2Ph(PPh_3)]$ decomposed selectively to toluene and $[AuMe(PPh_3)]$, indicating that the phenyl group is lost selectively in reductive elimination from gold(III). There is no general trend therefore, and the criterion should be applied with caution only when established by independent experiments with the metal ion under study.

If the above criteria are used, then *cis*-$[AuMe_2(4\text{-}MeC_6H_4)(PMe_2Ph)]$ and $[PtMe(4\text{-}MeC_6H_4)(COD)]$ appear to react with electrophiles by the S_E2 mechanism since aryl groups are cleaved selectively. This is fully consistent with the reactivity series $[PtMe(4\text{-}MeC_6H_4)(COD)]$ > $[Pt(4\text{-}MeC_6H_4)_2(COD)]$ > $[PtMe_2(COD)]$ although the range of reactivity is small. Thus the greater reactivity of the methyltolylplatinum(II) complex over the ditolylplatinum(II) complex is a result of the inductive effect of the methyl group increasing electron density on the aryl group.

Direct attack by electrophiles at the gold–carbon bond is expected since the filled d orbitals in $[AuMe_3L]$, L = tertiary phosphine, are 2–3 eV lower in energy than the gold–carbon σ MO's, as shown by photoelectron spectroscopy,[4,34] and because there are no precedents for oxidative additions of gold(III) to the very rare oxidation state gold(V).[35]

The selective cleavage of a methyl group from *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ or *cis*-$[PtMePh(PMePh_2)_2]$ can be taken as evidence for the S_E(oxidative) mechanism. However, this conclusion has been challenged recently,[15] and so a brief survey of the evidence is presented below.

Distinction between the S_E2 and S_E(oxidative) mechanisms cannot be made on the basis of kinetic rate law or of inductive effects of substituents on the ligands.[14] Thus, for example, electron-releasing substituents should increase the rate in either mechanism. Arguments against the S_E(oxidative) mechanism are based on the observation of the large kinetic isotope effect $k(H^+)/k(D^+)$ of 6–7 for protonolysis of an aryl–platinum bond in *cis*-$[PtAr_2(PEt_3)_2]$ or a methyl–platinum bond in *trans*-$[PtMeAr(PEt_3)_2]$. This is interpreted as showing rate-determining transfer of the proton to the aryl or methyl group and is considered to be inconsistent with a multistep S_E(oxidative) mechanism.[14,15] However, very similar isotope effects of $k(H)/k(D) \simeq 3$ are found for the concerted one-step reductive elimination of methane from *cis*-$[Pt(H \text{ or } D)Me(PPh_3)_2]$ and in multistep reactions where reductive coupling of alkyl and hydride from platinum(IV) is rate determining.[33,37] Thus the distinction between one-step and multistep mechanisms on the basis of isotope effects in related systems is not unambiguous, although the high values of $k(H)/k(D)$ in the protonolysis reactions do indicate that the proton must be about half-transferred in the transition state.[14,15]

Evidence in favor of the S_E(oxidative) mechanism can be listed as follows:

(1) It explains the selectivity result most readily.[16]

(2) It explains the reactivity series *cis*-$[PtMe_2L_2]$ > *cis*- or *trans*-$[PtMeArL_2]$ > *cis*- or *trans*-$[PtAr_2L_2]$. This is simply the sequence of reactivity toward oxidative addition. For

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(34) G. M. Bancroft, T. Chan, and R. J. Puddephatt, unpublished work.
(35) However, gold(IV) species have been proposed as transient intermediates.[36]
(36) S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Am. Chem. Soc.*, **99**, 8440 (1977).
(37) S. S. Moore, R. DiCosimo, A. F. Sowinski, and G. M. Whitesides, *J. Am. Chem. Soc.*, **103**, 948 (1981).

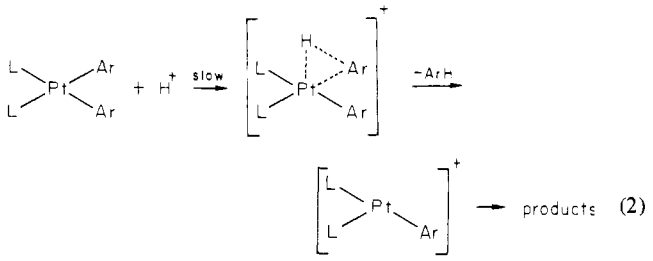
example, $[PtMe_2(bpy)]$ reacts over 100 times faster than $[PtPh_2(bpy)]$ (bpy = 2,2′-bipyridine) with methyl iodide.[38] This reactivity series is not expected if the S_E2 mechanism operates.

(3) In some closely related systems, the S_E(oxidative) mechanism can be proved directly by detection of the intermediate. An example with methyl iodide as electrophile was discussed above. Mercury(II) salts can oxidatively add to alkyl- or arylplatinum(II) complexes to give complexes such as IV or V.[39,40] In one case, subsequent transfer of a methyl group from platinum to mercury was demonstrated.[41] The exchange of D for H between DCl and *trans*-$[PtHCl(PEt_3)_2]$ involves an intermediate $[PtHDCl_2(PEt_3)_2]$, which can be detected in solution.[42,43]

Of course, it is possible that in these systems oxidative additions are particularly favorable and that in closely related systems the S_E2 mechanism may be favored. When the oxidized intermediate cannot be detected, the S_E(oxidative) mechanism must entail either rate-determining oxidative addition or a preequilibrium, with undetectably small concentration of oxidized intermediate, followed by rate-determining reductive elimination. It is here that distinction from the S_E2 mechanism is difficult.

(4) Studies of the photoelectron spectra of *cis*-$[PtMe_2L_2]$ (L = PMe_3 or PMe_2Ph) indicate that the Pt–C σ-bonding MO's lie 1.1–1.2 eV below the filled 5d orbitals.[4] Thus attack by electrophiles at platinum is expected on electronic grounds and should also be favored on steric grounds.

These indirect arguments can never be completely conclusive, but involvement of nonbonding d orbitals of platinum in reactions of $[PtR_2L_2]$ (L = tertiary phosphine) with electrophiles is strongly indicated. In order to rationalize the apparently conflicting evidence of the isotope effect it has been suggested that intermediate mechanisms between S_E2 and S_E(oxidative) may be possible as illustrated in eq 2 (Ar = aryl).[14,20]



(2)

Summary

We believe that the sharp change in selectivity between $[AuMe_2ArL]$ and $[PtMeArL_2]$ (L = phosphine ligand) is due to different mechanisms of reaction with electrophiles and that in the latter case the electrophile initially interacts with d orbitals on platinum. The result is nicely consistent with the observation from photoelectron spectra that in gold(III) the HOMO is an Au–C σ-bonding MO but in platinum(II) the HOMO is a nonbonding 5d orbital and with the known inability of gold(III) to undergo oxidative addition. The selectivity for [PtMeAr(COD)] could not be predicted in advance. Such complexes decompose before volatilization, and the photoelectron spectra cannot be obtained. Hence the relative energies of 5d orbitals and Pt–C σ-bonding MO's cannot be determined directly. However, the evidence is fully consistent with the S_E2 mechanism of electrophilic cleavage, and this can be rationalized, after the event, in terms of the known much lower reactivity of $[R_2Pt^{II}(COD)]$ complexes compared with $[R_2Pt^{II}(PR_3)_2]$ complexes toward oxidative addition.[18,31]

The observation that changing the neutral ligands in alkylarylplatinum(II) complexes can lead to quite different selectivity in Pt–C bond cleavage is significant since similar effects in catalytic reactions could well lead to different products being formed. Similar studies of selectivity toward insertion reactions should be particularly important.

Experimental Section

NMR spectra were recorded with a Perkin-Elmer R12B or Varian XL100 spectrometers. Phosphorus-31 chemical shifts are given with respect to $(MeO)_3PO$ reference.

$[PtI(4\text{-}MeC_6H_4)(COD)]$. This was prepared by reaction of $[PtI_2(COD)]$ (1.00 g) in CH_2Cl_2 (35 cm^3) with $[SnMe_3(4\text{-}MeC_6H_4)]$ (0.46 g). The mixture was heated under reflux for 16 h, the solvent was reduced in volume, and the product was precipitated as a yellow solid by addition of diethyl ether: yield 0.82 g, mp 174 °C dec. Anal. Calcd for $C_{15}H_{19}IPt$: C, 34.5; H, 3.6. Found: C, 34.2; H, 3.3. NMR ($CDCl_3$): δ(CH=) 5.86 (J(PtH) = 42.0 Hz) (trans to tolyl), 4.77 (J(PtH) = 74.4 Hz) (trans to I), $\delta(CH_2)$ 2.30, $\delta(CH_3)$ 2.20.

$[PtMe(4\text{-}MeC_6H_4)(COD)]$. To a solution of $[PtI(4\text{-}MeC_6H_4)(COD)]$ (1.05 g) in CH_2Cl_2 (30 cm^3) was added a solution of $AgNO_3$ (0.34 g) in methanol (15 cm^3) followed immediately by tetramethyltin (0.5 cm^3). After 5 min, the mixture was filtered to remove AgI and the solvent was evaporated to give the product, which was recrystallized from CH_2Cl_2–pentane: yield 0.85 g, mp 113–115 °C. Anal. Calcd for $C_{16}H_{22}Pt$: C, 47.0; H, 5.4. Found: C, 46.6; H, 5.25. NMR ($CDCl_3$): δ(CH=) 5.03 (J(PtH) = 56 Hz), 4.81 (J(PtH) = 55 Hz), $\delta(CH_2)$ 2.41, 2.27, $\delta(CH_3Pt)$ 0.82 (J(PtH) = 82.2 Hz), $\delta(CH_3C)$ 2.18.

***trans*-$[Pt(NO_3)(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$.** To a solution of *cis*-$[Pt(NO_3)_2(PMe_2Ph)_2]$ (2.00 g) in CH_2Cl_2 (30 cm^3) was added $[SnMe_3(4\text{-}MeC_6H_4)]$ (0.86 g). The mixture was heated under reflux for 1 day. The volume of solution was reduced to yield white crystals of the product, which were washed thoroughly with ether: yield 1.95 g, mp 114–116 °C. Anal. Calcd for $C_{23}H_{29}NO_3P_2Pt$: C, 44.2; H, 4.4; N, 2.2. Found: C, 44.6; H, 4.7; N, 2.0. NMR ($CDCl_3$): δ(MeP) 1.28 (t, $^2J + {}^4J$(PH) = 7.2 Hz, ^3J(PtH) = 34.2 Hz), δ(MeC) 1.97. Similarly, *trans*-$[Pt(NO_3)Ph(PMePh_2)_2]$ was prepared from *cis*-$[Pt(NO_3)_2(PMePh_2)_2]$ and $SnMe_3Ph$.

***cis*-$[PtMePh(PMePh_2)_2]$.** Methyllithium in diethyl ether (2.0 cm^3, 1.5 M solution) was added slowly to a suspension of *trans*-$[Pt(NO_3)Ph(PMePh_2)_2]$ (1.74 g) in diethyl ether (50 cm^3) under an atmosphere of N_2, and the mixture was stirred for 30 min at room temperature. The mixture was hydrolyzed, the ether layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2 (20 cm^3). The dried combined organic extracts were evaporated under vacuum to give the product as a white solid, mp 47–52 °C. Anal. Calcd for $C_{33}H_{34}P_2Pt$: C, 57.6; H, 5.0. Found: C, 55.9; H, 5.0. ^{1}H NMR (CD_2Cl_2): δ(MeP) 1.50 (d, ^2J(PH) = 7.0 Hz, ^3J(PtH) = 19 Hz), 1.32 (d, ^2J(PH) = 8.0 Hz, ^3J(PtH) = 23 Hz), δ(MePt) 0.36 (dd, ^3J(PH) = 7.0 Hz, 9.0 Hz, ^2J(PtH) = 70 Hz). ^{31}P{^{1}H} NMR in CH_2Cl_2: $\delta(^{31}P)$ 1.69 (^2J(PP) = 12.37 Hz, ^1J(PtP) = 1837 Hz), 0.37 (^1J(PtP) = 1757 Hz).

Similarly, *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ was prepared from *trans*-$[Pt(NO_3)(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ as a colorless oil. Anal. Calcd for $C_{24}H_{30}P_2Pt$: C, 49.9; H, 5.2. Found: C, 49.5, H, 5.1. ^{1}H NMR (CH_2Cl_2) δ(MeP) 1.37 (d, ^2J(PH) = 7.8 Hz, ^3J(PtH) = 20 Hz), 1.72 (d, ^2J(PH) = 8.4 Hz), ^3J(PtH) = 22 Hz), δ(MePt) 0.31 (dd, ^3J(PH) = 6.0 Hz, 7.2 Hz, ^2J(PtH) = 70 Hz).

***cis*-$[AuMe_2(4\text{-}MeC_6H_4)(PPh_3)]$.** To a suspension of *cis*-$[AuClMe_2(PPh_3)]$ (0.80 g) suspended in diethyl ether (15 mL) was added dropwise 4-MeC_6H_4MgBr in diethyl ether (5 mL, 0.31 M solution). After 30 min at room temperature, the mixture was hydrolyzed and the product was isolated. It gave white crystals from ether–pentane: yield 0.72 g, mp 100–102 °C. Anal. Calcd for $C_{27}H_{28}AuP$: C, 55.9; H, 4.9. Found: C, 56.0; H, 4.8. ^{1}H NMR (CH_2Cl_2): δ(MeAu) 1.07 (d, ^3J(PH) = 9.6 Hz), 0.13 (d, ^3J(PH) = 6.6 Hz), δ(MeC) 2.13 (s).

Similarly, *cis*-$[AuMe_2Ph(PPh_3)]$ was prepared from *cis*-$[AuClMe_2(PPh_3)]$ and PhMgBr; mp 97–101 °C. NMR (CH_2Cl_2):

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δ(MeAu) 0.36 (d, ^3J(PH) = 7.0 Hz) (trans to Ph), 1.30 (d, ^3J(PH) = 10.0 Hz) (trans to PPh_3), δ(^{31}P) 23.49.

***cis*-[PtMe(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] with HCl.** A solution of HCl in ether (1.2 mL, 1.06 M) was added dropwise by syringe to a solution of *cis*-[PtMe(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] (0.045 g) in ether (2 mL) cooled to −78 °C in a flask (10 mL) fitted with serum cap. The solution was allowed to warm to room temperature. A gas was evolved and a white solid precipitated. The gas was shown to be methane (GC–MS). The solvent was evaporated to give *cis*-[PtCl(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$], pure on the basis of NMR spectroscopy. A sample was recrystallized rapidly from CH_2Cl_2–pentane: yield 86%; mp 138–140 °C. Anal. Calcd for $C_{23}H_{29}ClP_2Pt$: C, 46.35; H, 4.57. Found: C, 46.91; H, 5.34. NMR ($CDCl_3$): δ(MeP) 1.65 (d, ^2J(PH) = 11 Hz, ^3J(PtH) = 36 Hz) (trans to Cl), 1.46 (d, ^2J(PH) = 9 Hz, ^3J(PtH) = 17 Hz) (trans to tolyl), δ(MeC) 2.14.

Other reactions with hydrogen chloride (Table I) were carried out in a similar way.

[PtMe(4-MeC$_6$H$_4$)(COD)] with HgCl$_2$. A solution of $HgCl_2$ (0.021 g) in methanol (5 mL) was added slowly to a solution of [PtMe(4-MeC$_6$H$_4$)(COD)] (0.031 g) in ether (2 mL). After 30 min, the solvents were evaporated and the products identified as [PtClMe(COD)] and [HgCl(4-MeC$_6$H$_4$)] by the characteristic ^{1}H NMR spectra. The identification was confirmed by TLC on silica eluting with $CHCl_3$, by comparison with authentic samples. In particular, [HgClMe] and [PtCl(4-MeC$_6$H$_4$)(COD)] were shown to be absent by NMR spectroscopy and TLC. NMR ($CDCl_3$): δ(CH=) 5.64 (s, ^2J(PtH) = 38 Hz) (trans to Me), 4.56 (s, ^2J(PtH) = 78 Hz) (trans to Cl), δ(CH_2) 2.40, 2.30 (s), δ(MePt) 1.24 (s, ^2J(PtH) = 78 Hz).

Other reactions with $HgCl_2$ were carried out in a similar way (Table I).

[PtMe(4-MeC$_6$H$_4$)(COD)] with [PtI$_2$(PMe$_2$Ph)$_2$]. [PtMe(4-MeC$_6$H$_4$)(COD)] (0.035 g) and [PtI$_2$(PMe$_2$Ph)$_2$] (0.062 g) were dissolved in $CDCl_3$ (0.60 mL), and the solution was sealed in an NMR tube, which was then kept in the dark in a thermostated bath at 25 °C. The mixture reacted slowly to give [PtIMe(COD)] and *trans*-[PtI(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$]. The rate of reaction was monitored by studying the decay of the MePt resonance of [PtMe(4-MeC$_6$H$_4$)(COD)] in the NMR spectrum as a function of time. The products were identified by comparison of spectra with those of authentic compounds. For this purpose, *trans*-[PtI(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] was prepared by reaction of *trans*-[Pt(NO$_3$)(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] (0.133 g) in CH_2Cl_2 (10 mL) with sodium iodide (1.0 g) in water (10 mL). The organic layer was dried and evaporated to give the product, mp 140–142 °C. Anal. Calcd for $C_{23}H_{29}IP_2Pt$: C, 40.1; H, 3.9. Found: C, 40.0; H, 4.0. NMR ($CDCl_3$): δ(MeP) 1.53 (t, $^2J + {}^4J$(PH) = 6.6 Hz, ^3J(PtH) = 32 Hz).

Other reactions with transition metal halides as reagents were carried out in a similar way (Table I).

***cis*-[PtMe(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] with Methyl Iodide.** Methyl iodide (0.5 mL) was added to a solution of *cis*-[PtMe(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] (0.075 g) in CH_2Cl_2 (10 cm^3). After 10 min, the volume was reduced, pentane was added, and the solution was allowed to stand at 0 °C to give crystals of [PtIMe$_2$(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$]: yield 87%; mp 62–64 °C dec. Anal. Calcd for $C_{25}H_{35}IP_2Pt$: C, 41.7; H, 4.9. Found: C, 40.8; H, 5.0. NMR ($CDCl_3$): δ(MePt) 0.72 (^3J(PH) = 7 Hz, ^2J(PtH) = 68 Hz), 1.10 (m, ^2J(PtH) = 60 Hz), δ(MeP) 1.50, 1.54 (d, ^2J(PH) = 7 Hz, ^3J(PtH) = 11 Hz).

A sample of this product (0.03 g) in a small tube fitted with a septum was heated to the decomposition point. The gas evolved was shown to be pure ethane by GC–MS. The residue was then identified as *trans*-[PtI(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$] by the NMR spectrum.

Thermal Decomposition of *cis*-[AuMe$_2$Ph(PPh$_3$)]. A solution of *cis*-[AuMe$_2$Ph(PPh$_3$)] (0.145 g) in benzene (0.5 mL) was sealed in a thick-walled NMR tube, and the subsequent decomposition was monitored with ^{1}H and ^{31}P NMR spectroscopy. No decomposition occurred on heating to 50 °C for 4 h, but at 80 °C decomposition to toluene and [AuMe(PPh$_3$)] was complete in 1 h. No ethane was detected. The tube was opened, and the volatiles were distilled under vacuum into a second NMR tube. The ^{1}H NMR spectrum confirmed the presence of toluene (δ(Me) 2.10). The white solid residue was washed with methanol, dried under vacuum, and dissolved in CD_2Cl_2. The NMR spectra confirmed that this was [AuMe(PPh$_3$)]: δ(MeAu) 0.57 (d, ^3J(PH) = 8 Hz, δ(^{31}P) 44.1 (s). An authentic specimen gave identical spectral parameters.

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Registry No. *cis*-[AuMe$_2$Ph(PPh$_3$)], 42029-61-8; *cis*-[AuMe$_2$(4-MeC$_6$H$_4$)(PPh$_3$)], 66485-01-6; PtMe(4-MeC$_6$H$_4$)(COD), 66485-00-5; *cis*-[PtMePh(PMePh$_2$)$_2$], 75095-27-1; *cis*-[PtMe(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$], 66484-99-9; PtI(4-MeC$_6$H$_4$)(COD), 60751-01-1; *trans*-[Pt(NO$_3$)(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$], 79735-34-5; PtI$_2$(COD), 12266-72-7; *cis*-[Pt(NO$_3$)$_2$(PMe$_2$Ph)$_2$], 58320-37-9; *trans*-[Pt(NO$_3$)Ph(PMePh$_2$)$_2$], 79723-35-6; *cis*-[AuClMe$_2$(PPh$_3$)], 33635-50-6; *cis*-[PtCl(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$], 66537-46-0; PtClMe(COD), 50978-00-2; PtI$_2$(PMe$_2$Ph)$_2$, 15616-82-7; *trans*-[PtI(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$, 61483-40-7; PtIMe$_2$(4-MeC$_6$H$_4$)(PMe$_2$Ph)$_2$, 66559-65-7; AuMe(PPh$_3$), 23108-72-7; PtCl$_2$(COD), 12080-32-9; *cis*-[AuIMe$_2$(PPh$_3$)], 34275-48-4; PtCl(4-MeC$_6$H$_4$)(COD), 57110-60-8; AuI(PPh$_3$), 21209-78-9; *trans*-[PtIMe(PMe$_2$Ph)$_2$], 24882-77-7; *cis*-[PdCl$_2$(PMe$_2$Ph)$_2$], 29484-66-0; AuCl(PMePh$_2$), 38686-38-3; *trans*-[PdClMe(PMe$_2$Ph)$_2$], 30179-98-7; AuMe(PMePh$_2$), 52170-95-3; *cis*-[PtClPh(PMePh$_2$)$_2$], 79767-75-2; PtIMe(COD), 53789-87-0; Pt(NO$_3$)Me(COD), 79721-40-7; AuMe$_3$(PMe$_2$Ph), 54854-73-8; *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$], 24917-48-4; *trans*-[Pt(4-MeC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$], 79721-41-8; PtMe$_2$(COD), 12266-92-1; Pt(4-MeC$_6$H$_4$)$_2$(COD), 54866-11-4; SnMe$_3$(4-MeC$_6$H$_4$), 937-12-2; SnMe$_4$, 594-27-4; SnMe$_3$Ph, 934-56-5; 4-MeC$_6$H$_4$Br, 106-38-7; PhBr, 108-86-1; HgCl$_2$, 7487-94-7; HgCl(4-MeC$_6$H$_4$), 539-43-5; HgClMe, 115-09-3; MeI, 74-88-4.