Complexes with PtAu and PtAg Bonds: Catalysis by Silver(I) of Alkyl Exchange Reactions between Platinum Centers

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The electron-rich platinum(II) complex [PtMe$_2$(2,2′-bpy)] (1, bpy = bipyridine) reacts with [Au(NO$_3$)(PPh$_3$)], [Au(BF$_4$)(PPh$_3$)], [Au(PF$_6$)(PPh$_3$)], [Ag(BF$_4$)(PPh$_3$)], and AgBF$_4$ to give the Pt–M bonded complexes [PtMe$_2$(bpy)(AuPPh$_3$)]NO$_3$ (**3a**), [PtMe$_2$(bpy)(AuPPh$_3$)]BF$_4$ (**3b**), [PtMe$_2$(bpy)(AuPPh$_3$)]PF$_6$ (**3c**), [PtMe$_2$(bpy)(AgPPh$_3$)]BF$_4$ (**3d**), and [{PtMe$_2$(bpy)}$_2$Ag]BF$_4$ (**4**), respectively. These compounds are shown to contain PtAu or PtAg bonds by their ^{1}H, ^{31}P, and ^{195}Pt NMR spectroscopic properties. Complexes **3c** and **4** were isolated in analytically pure form, but **3a**, **3b**, and **3d** were too unstable thermally to characterize by elemental analysis. The Pt–Au bonded complexes appear to be the first such binuclear complexes to have been characterized unambiguously. Decomposition of the complexes occurs with formation of Ag or Au metal and equimolar amounts of Me$_3$Pt^{IV} and MePt^{II} derivatives. AgBF$_4$ catalyzes the exchange of CH$_3$ and CD$_3$ groups between [PtMe$_2$(bpy)] and [Pt(CD$_3$)$_2$(bpy)], as analyzed by MS, or between [PtMe$_2$(1,10-phen)] (phen = phenanthroline) and [Pt(CD$_3$)$_2$(bpy)], as analyzed by ^{1}H NMR.

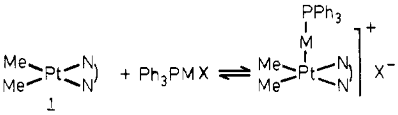
Introduction

There has been much recent interest in complexes with PtAg and PtAu bonds. Most such compounds are clusters, with PtAu$_2$,[1] Pt$_2$Au,[2] Pt$_2$Au$_2$,[3] Pt$_3$Au,[4] Pt$_3$Au$_2$,[5] PtAu$_6$,[6] and PtAu$_7$[7] clusters all having been prepared since 1984. Several unusual PtAg bonded complexes have been characterized also,[8–11] including one complex [(C$_6$F$_5$)$_3$(SC$_4$H$_8$)PtAgPPh$_3$] with a covalent PtAg bond and no supporting bridging ligands.[9] No analogous binuclear PtAu bonded complexes are well characterized, although there is an early claim for the complex [(Ph$_3$P)$_2$ClPtAuPPh$_3$].[12] The chemistry of gold–metal bonded complexes has been reviewed.[13]

It has been shown that electrophilic gold fragments, Ph$_3$PAu$^+$ or ClAu which are isolobal with H$^+$, can be added to electron-rich binuclear or trinuclear platinum complexes to yield Pt$_2$Au or Pt$_3$Au clusters respectively.[2,4] This work explores similar attempts to prepare PtAu or PtAg complexes by addition of electrophilic gold or silver fragments to an electron-rich mononuclear platinum(II) precursor. The complex studied was [PtMe$_2$(2,2′-bpy)] which has been shown to be one of the most reactive species in oxidative addition chemistry and hence is a powerful metal-based nucleophile.[14] It also offers the possibility of further organometallic chemistry of the products, involving methyl group migration between metal centers. Intermolecular migration of methyl groups between platinum and gold centers has been observed previously,[15] and this work gives useful insights into the mechanism of such reactions.

Results and Discussion

Formation of Complexes [PtMe$_2$(bpy)(MPPh$_3$)]$^+$. Reaction of the electron-rich [PtMe$_2$(2,2′-bpy)] (1) with [Ph$_3$PAuNO$_3$)] in dichloromethane solution gave an adduct, **3a**, which could be isolated as a thermally unstable red oil, (eq 1). Similar complexes, **3b** and **3c**, with almost identical spectroscopic properties, were formed on reaction of 1 with [Ph$_3$PAuBF$_4$] and [Ph$_3$PAuPF$_6$], respectively, and a still less stable adduct, **3d**, was formed by reaction of 1 with [Ph$_3$PAgBF$_4$] (eq 1). Of these complexes **3**, only the hexafluorophosphate salt **3c** could be crystallized in pure form. The other complexes were too unstable to give good analytical data, but they were spectrosopically pure and were characterized by multinuclear NMR spectroscopy, by conductivity measurements, and by their chemical reactions.



(1)

The molar conductivities of **3a**, **3b**, and **3c** in acetone solution (2 × 10^{-3} M) at 20 °C were 36, 44, and 130 cm^2 Ω^{-1} M^{-1}, respectively, indicating the ionic nature of the products. The values for **3a** and **3b** are lower than expected for 1:1 electrolytes, which we attribute to ion pairing effects.[17] Although an equilibrium with neutral

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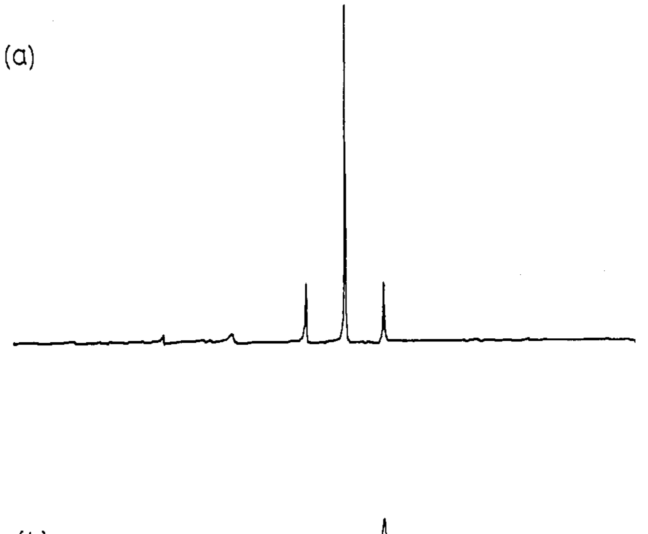

Figure 1. NMR spectra of $[PtMe_2(bpy)(AuPPh_3)]^+$ in $CDCl_3$ at -60 °C: (a) $^{31}P\{^1H\}$ spectrum (121.5 MHz), $\delta(P)$ 4.2 [$^2J(PtP)$ = 1250 Hz]; (b) $^{195}Pt\{^1H\}$ spectrum (64.3 MHz), $\delta(Pt)$ 1360 [$^2J(PtP)$ = 1250 Hz]. For each spectrum the width of plot is 10000 Hz.

$[PtMe_2(AuPPh_3)X(bpy)]$ cannot be ruled out when X = NO_3, the observation of essentially identical NMR properties of complexes **3a–c**, together with the observation below that coordinating ligands decompose the adducts, strongly suggests the ionic form shown in all cases. An analogous ionic five-coordinate iridium complex, $[Ir(Ph_2PCH_2CH_2PPh_2)_2(AuPPh_3)]^{2+}$, and a neutral five-coordinate platinum complex, $[(C_6F_5)_3(C_4H_8S)Pt(AgPPh_3)]$, very similar to **3d**, have been characterized crystallographically.[9,16] However, **3a–c** appear to be the first examples of binuclear complexes for which there is direct evidence for the presence of PtAu bonds.

In the ^1H NMR spectrum of **3a**, the coupling constant $^2J(PtCH_3)$ = 64 Hz was much reduced from the value of 86 Hz for **1**. Reductions of this order are observed on oxidation of **1** to octahedral platinum(IV) derivatives or on formation of adducts of coordination number five and so are fully consistent with the structures **3**.[18] In particular, a very similar change is observed in the complex $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, which contains a donor–acceptor metal–metal bond from a $PtMe_2L_2$ unit to a $PtMeL_2^+$ acceptor.[18] The $^{31}P\{^1H\}$ NMR spectrum of **3a** or **3b** at room temperature contained only a broad singlet, but this became a sharp singlet with ^{195}Pt satellites at low temperature (Figure 1). This observation suggests that the equilibrium of eq 1 is fast on the NMR time scale at room temperature and the coupling $^2J(PtP)$ is not observed in the fast-exchange regime.[19] Confirmation was obtained by addition of excess Ph_3PAuNO_3 (**2a**), to a solution of **3a**. At low temperature, separate ^{31}P NMR signals due to **2a** and **3a** were observed as expected (eq 1), but only a broad average signal was observed at room temperature. Since the ^{31}P chemical shift of pure **3a** was essentially independent of temperature, the equilibrium of eq 1 must lie well to the right even at room temperature. The $^{195}Pt\{^1H\}$ NMR spectrum of **3a** at low temperature contained only a doublet with $^2J(PtAuP)$ = 1250 Hz, confirming the presence of a single Ph_3PAu unit in **3a** (Figure 1).

The adducts **3** were only formed if a weakly coordinating group X was present on gold. Thus $[AuCl(PPh_3)]$ failed to react with **1**. In addition, reaction of **3a** with Cl^- or PPh_3 gave back **1** and $[AuCl(PPh_3)]$ or $[Au(PPh_3)_2]^+$, respectively, in quantitative yields. It is clear therefore that the electron-rich platinum center of **1** is acting as a donor ligand for gold in forming the adducts **3** and can only compete if X^- is a poor ligand for gold. Thus the donor ability to gold is found to be $Ph_3P > Cl^- >$ complex **1** $> NO_3^- > BF_4^-$, as a result of the above and previously obtained data.[18]

Solutions of **3d** slowly deposited a silver mirror even at -70 °C, and pure samples could not be isolated. Characterization in this case was aided by the presence of ^{107}Ag and ^{109}Ag each having spin $I = {}^1/_2$. The ^{31}P and ^{195}Pt NMR spectra of **3d** at -70 °C gave couplings $^1J(^{107}AgP)$ = 606 Hz and $^1J(^{109}AgP)$ = 676 Hz, mean $^1J(^{107}AgPt, ^{109}AgPt)$ = 680 Hz,[20] thus proving the presence of the $PtAgPPh_3$ unit. In the ^1H NMR spectrum at -70 °C, the coupling of $^3J(AgPtCH_3) \approx 3$ Hz,[21] as well as the coupling $^2J(PtCH_3)$ = 75 Hz, was resolved for the methylplatinum resonance. Thus the structure **3d** is confirmed.

Reactions Leading to Methyl Group Transfer. In several cases, attempts to prepare complexes with PtAu, PtAg or PtCu bonds were unsuccessful, but a type of disproportionation occurred. For example, the reaction of *1* with $[AuCl(SMe_2)]$, which was carried out with the hope of preparing $[PtMe_2(bpy)(AuCl)]$, occurred instead according to eq 2.

$$2[PtMe_2(bpy)] + 2[AuCl(SMe_2)] \rightarrow [PtClMe_3(bpy)] + [PtClMe(bpy)] + 2Au + 2SMe_2 \quad (2)$$

The same products were observed in $CHCl_3$, CH_2Cl_2, or acetone solvents and whether oxygen was present or absent. The same platinum products were obtained along with copper metal from reaction of **1** with CuCl in acetone, but in CH_2Cl_2 two isomers[22] of $[PtMe_2Cl(CH_2Cl)(bpy)]$ were also formed. In this case the copper reagent evidently also catalyzes the oxidative addition of CH_2Cl_2 to **1**, since this reaction is slow in the absence of CuCl.[22]

The decomposition products of **3c** were identified as *fac*-$[PtMe_3(bpy)(PPh_3)]^+$ and $[PtMe(PPh_3)(bpy)]^+$. Thus, the oxidation of Pt(II) to Pt(IV), with transfer of a methyl

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(17) This is a well-known phenomenon. See, for example: Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637. The difficulty of purifying the oils may also contribute to the low values of **3a** and **3b**.

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(19) A reviewer suggested that the fluxionality may involve a unidentate bpy ligand. This is ruled out by the low-temperature ^1H NMR spectra which show clearly the equivalence of the two C_5H_4N rings.

(20) The ^{195}Pt resonance was broad, and the expected separate couplings $J(^{107}AgPt)$ and $J(^{109}AgPt)$ were not resolved. $^1J(PtAg)$ couplings have been observed previously.[10,11]

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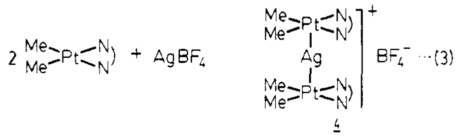
group from a further molecule of 1 to Pt(IV), leads to equimolar amounts of *fac*-Me_3Pt^{IV} and $MePt^{II}$ units in all of the above reactions. The mechanism of reaction is unknown.

Reaction of [PtMe$_2$(bpy)] with AgBF$_4$. This reaction, carried out in acetone at −70 °C, gave a red precipitate which analyzed as $\{PtMe_2(bpy)\}_2AgBF_4$. The stoichiometry was confirmed by addition of aliquots of $AgBF_4$ to a solution of $[PtMe_2(bpy)]$ in acetone-d_6, monitoring by ^1H NMR. After addition of 0.5 molar equiv of $AgBF_4$, the resonances due to $[PtMe_2(bpy)]$ were absent. Addition of excess NaCl to the above mixture gave a precipitate of AgCl, and $[PtMe_2(bpy)]$ was regenerated.

The red precipitate was characterized as the sandwich complex 4 (eq 3) from the stoichiometry of reaction and the NMR parameters. It is stable as a solid, but in acetone solution it decomposes to give a silver mirror on warming to room temperature. The ^1H NMR spectrum gave a methylplatinum resonance, whose appearance was temperature-dependent. At −90 °C, the resonance was at δ 0.78 [$^2J(PtH) = 68$ Hz], at −80 °C, the resonance was at δ 0.86 [$^2J(PtH) = 65$ Hz], but at −40 °C the resonance was at δ 0.95 with no resolved satellites due to coupling to ^{195}Pt. At −90 °C, the ^{195}Pt NMR spectrum gave a broad resonance at δ 439 with no detectable coupling $^1J(AgPt)$.



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These data suggest that the equilibrium of eq 3 is rapid even at −90 °C. However, the loss of the $^2J(PtCH_3)$ coupling is novel and suggested that reversible cleavage of $PtCH_3$ bonds might also be occurring at temperatures above −40 °C. This was confirmed by reaction of a mixture of $[Pt(CH_3)_2(bpy)]$ and $[Pt(CD_3)_2(bpy)]$ with $AgBF_4$, followed by reaction with NaCl to give back the starting material. Mass spectral analysis gave the relative abundances of $[Pt(CH_3)_2(bpy)]$:$[Pt(CH_3)(CD_3)(bpy)]$:$[Pt(CD_3)_2(bpy)]$ = 1.3:2.1:1.0, indicating complete scrambling of CH_3 and CD_3 groups. The same reaction in the absence of $AgBF_4$ gave apparent partial scrambling, with the corresponding ratio being 2.1:1.0:1.8. Suspecting that this scrambling may occur in the mass spectrometer probe, an additional experiment with $[Pt(CH_3)_2(phen)]$, with and without $AgBF_4$ present, was carried out, with monitoring of the reaction by ^1H NMR. Without $AgBF_4$ no scrambling was observed after 2 h, but addition of a catalytic quantity of $AgBF_4$ gave signals due to both $[Pt(CH_3)(CD_3)(bpy)]$ {δ 0.95 [$^2J(PtH) = 86$ Hz]} and $[Pt(CH_3)(CD_3)(phen)]$ {δ 1.11 [$^2J(PtH) = 85$ Hz]}, indicating that methyl scrambling occurred. Previously studies have been unsuccessful, in detecting methyl for methyl exchange between platinum complexes.

Conclusions

The data above show that $[PtMe_2(bpy)]$ can form complexes with 1:1 stoichiometry with Ph_3PAu^+ or Ph_3PAg^+ or with 2:1 stoichiometry with Ag^+. These are formed presumably by initial donation from the filled d_{z^2} orbital of platinum to a vacant sp hybrid orbital on silver(I) or gold(I), though the presence of substantial $^1J(PtAg)$ or $^2J(PtAuP)$ couplings in the adducts 3 clearly indicates that the PtM bond uses an orbital on platinum with substantial s character. This is also indicated by the decrease in coupling constant $^2J(PtCH_3)$ from 86 Hz in 1 to 64–75 Hz in the adducts 3 or 4. Thus rehybridization at platinum accompanies Pt–M bond formation.

The complexes formed are of much lower thermal stability compared to known compounds such as $[Pt(C_6F_5)_3(C_4H_8S)(AgPPh_3)]$.[9] This low thermal stability is evidently due to the presence of methylplatinum groups in 3 or 4 rather than the more inert (pentafluorophenyl)platinum groups. As a result these new complexes could not be characterized crystallographically. However, there are compensating benefits from the presence of the methylplatinum groups since it is shown that Ag^+ can catalyze the exchange of methyl groups between platinum atoms in a remarkable way. If this occurs, as appears probable, by rapid reversible transfer of methyl groups between platinum and silver[23] then, since methylsilver groups are generally more reactive than methylplatinum groups, it may be possible to catalyze many organometallic reactions of methylplatinum complexes by silver(I). Complexes similar to 3 have been postulated as intermediates in the methyl-transfer reactions between *cis*-$[PtMe_2(PR_3)_2]$ and $[AuCl(PR_3)]$ to give an equilibrium with *trans*-$[PtClMe(PR_3)_2]$ and $[AuMe(PR_3)]$,[15] and this work shows the plausibility of such a mechanism. Clearly reductive elimination from 3 would give $[AuMe(PPh_3)]$ and $[PtMeX(bpy)]$, though this step is not favorable with the 2,2′-bipyridine complexes. Similar metal–metal interactions have been proposed in the intermolecular coupling of methyl groups in methylgold(I) complexes.[24] Complexes 3 can also be regarded as isolobal analogues of intermediates $[PtMe_2HL_2]^+$, proposed as intermediates in the protonolysis of methylplatinum bonds in *cis*-$[PtMe_2L_2]$.[25,26]

In conclusion, this work has led not only to some of the simplest donor–acceptor metal–metal bonded complexes but also to the discovery of remarkably easy, silver(I)-catalyzed, methyl for methyl exchange on platinum(II).

Experimental Section

NMR spectra were recorded by using a Varian XL200 or XL300 spectrometer, with Me_4Si, H_3PO_4, and K_2PtCl_4 as references for ^1H, ^{31}P, and ^{195}Pt, respectively. $[PtMe_2(bpy)]$ was prepared by the literature method.[18]

[PtMe$_2$(bpy)(AuPPh$_3$)]NO$_3$ (3a). To a solution of $[PtMe_2(bpy)]$ (15 mg, 0.04 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added $[Au(NO_3)(PPh_3)]$ (20.8 mg, 0.04 mmol) in CH_2Cl_2 (4 mL). There was an immediate color change from red to yellow. The solvent was removed to yield a red oil, which could not be induced to crystallize and which decomposed rapidly at room temperature. NMR in $CDCl_3$: ^1H, δ 1.55 [s, 6 H, $^2J(PtH) = 64$ Hz, Pt*Me*]; ^{31}P (−60 °C), δ 4.2 [s, $^2J(PtP) = 1250$ Hz, *P*Au]; ^{195}Pt, (−60 °C), δ 1360 [d, $^2J(PtP) = 1250$ Hz, Pt].

Complex 3b was prepared similarly, using $[Au(BF_4)(PPh_3)]$, freshly prepared from $[AuCl(PPh_3)]$ and $AgBF_4$. The NMR spectra were identical with those of 3a.

Complex 3a and excess $[Au(NO_3)(PPh_3)]$ (25 mol %) were mixed. NMR: ^{31}P (20 °C), δ 7.26 (br s, average PAu); ^{31}P (−60 °C), δ 4.2 [s, $^2J(PtP) = 1250$ Hz, *P*AuPt of 3a], 21.1 (s, *P*Au of Ph_3PAuNO_3).

[PtMe$_2$(bpy)(AuPPh$_3$)]PF$_6$ (3c). To a solution of $[PtMe_2(bpy)]$ (21 mg) in CH_2Cl_2 (8 mL) at 0 °C was added dropwise a cold, filtered solution of $Au(PF_6)PPh_3$, freshly prepared by reaction

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(23) An alternative might involve single electron transfer to the group 11 element, followed by further rapid reactions of the $[PtMe_2(bpy)]^{\bullet+}$ cation radical. However, oxidation of $[PtMe_2L_2]$ (L = phosphine) by $[IrCl_6]^{2-}$ is thought to occur in this way and does not appear to give methyl exchange reactions of the type described in this paper. Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450.

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(26) For a discussion of the isolobal analogy between LAu^+ and H^+, see: Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648.

of $AgPF_6$ (14.2 mg) in CH_3OH (10.5 mL) with $[AuCl(PPh_3)]$ (27.8 mg) in acetone (4 mL). The solvent volume was reduced under vacuum, and the product was precipitated with ether (25 mL), washed with pentane (20 mL) at 0 °C, and dried under high vacuum. Anal. Calcd for $C_{30}H_{29}AuF_6N_2P_2Pt$: C, 36.6; H, 3.0; N, 2.9. Found: C, 36.3; H, 2.75; N, 2.7%. NMR (−60 °C): ^1H, δ 1.28 [s, $^2J(PtH)$ = 68 Hz, MePt]; ^{31}P, δ 3.9 [s, $^2J(PtP)$ = 1250 Hz, *P*AuPt].

Reactions of Complex 3a. To a solution of **3a** (6 mg) in acetone (4 mL) was added KCl (2 mg) in water (1 mL). The solvents were evaporated under vacuum and the products identified by NMR: $[PtMe_2(bpy)]$, ^1H, δ 0.95 [s, $^2J(PtH)$ = 86 Hz, Pt*Me*]; $[AuCl(PPh_3)]$, ^{31}P, δ 26.6 [s, *P*Au]. The reaction of **3a** with PPh_3 to give $[PtMe_2(bpy)]$ and $[Au(PPh_3)_2]NO_3$ [^{31}P, δ 37.6 (*P*Au)] was carried out in a similar way.

$[PtMe_2(bpy)(AgPPh_3)]BF_4$ (3d). To a solution of $[PtMe_2(bpy)]$ (8.0 mg, 0.021 mmol) in acetone-d_6 (0.5 mL) at −70 °C was added slowly a solution of Ph_3P (6.0 mg, 0.023 mmol) and $AgBF_4$ (4.5 mg, 0.023 mmol) in acetone-d_6 (0.05 mL). A color change from red to yellow was observed. NMR in acetone-d_6: ^1H (−70 °C), δ 1.13 [d, 6 H, $^2J(PtH)$ = 75, $^3J(AgH)$ = 2 Hz, Pt*Me*]; ^{31}P (−80 °C), δ −0.5 [d × 2, $^1J(^{107}AgP)$ = 606, $^1J(^{109}AgP)$ = 676 Hz]; ^{195}Pt (−80 °C), δ 475 [d, br, $^1J(AgPt)$ = 680 Hz, average of $^1J(^{107}AgPt)$ and $^1J(^{109}AgPt)$].

When the above solution was allowed to warm to room temperature, a silver mirror was deposited. The solution then contained *fac*-$[PtMe_3(PPh_3)(bpy)]^+$ [NMR: ^1H, δ 1.37 [d, $^3J(PH)$ = 8, $^2J(PtH)$ = 68 Hz, *Me*Pt trans to bpy], 0.53 [d, $^3J(PH)$ = 7.5, $^2J(PtH)$ = 60 Hz, *Me*Pt trans to P]; ^{31}P, δ −8.5 [s, $^1J(PtP)$ = 1045 Hz, Pt*P*] and $[PtMe(PPh_3)(bpy)]^+$ [NMR: ^1H, δ 0.80 [d, $^3J(PH)$ = 3.5 Hz, $^2J(PtH)$ = 71.5 Hz, *Me*Pt]; ^{31}P, δ 15.0 [s, $^1J(PtP)$ = 4340 Hz, Pt*P*]].

$[PtMe_2(bpy)]$ with $[AuCl(SMe_2)]$. To a solution of $[PtMe_2(bpy)]$ (8.6 mg, 0.023 mmol) in CD_2Cl_2 (0.3 mL) at −70 °C was added a solution of $[AuCl(SMe_2)]$ (8.7 mg, 0.029 mmol) in CD_2Cl_2 (0.3 mL). The ^1H NMR spectrum at −40 °C showed that no reaction had occurred. At −10 °C, a gold mirror was formed and the solution contained equimolar amounts of $[PtClMe_3(bpy)]$ and $[PtClMe(bpy)]$, identified by their NMR spectra by comparison with authentic samples. The same products were formed in acetone-d_6 solvent. A similar reaction with excess CuCl in acetone at room temperature gave the same products and copper metal, but in CH_2Cl_2 the known isomers of $[PtMe_2Cl(CH_2Cl)(bpy)]$ and some $[PtMe_2Cl_2(bpy)]$ were also formed. Again no PtCu-bonded intermediates were detected.

$[\{PtMe_2(bpy)\}_2Ag]BF_4$ (4). To a solution of $[PtMe_2(bpy)]$ (71 mg, 0.186 mmol) in acetone (10 mL) at −70 °C was added $AgBF_4$ (18.4 mg, 0.094 mmol) in acetone (5 mL). A red precipitate formed immediately. After 15 min the solvent was removed and the precipitate was washed with acetone/ether (10 mL, 1:1) at −70 °C and then with ether at 20 °C and dried under vacuum: yield 74 mg; mp 145–152 °C dec. Anal. Calcd for $C_{24}H_{28}AgBF_4N_4Pt_2$: C, 30.1; H, 2.95; N, 5.85. Found: C, 30.2; H, 3.2; N, 5.9. NMR in acetone-d_6: ^1H (−80 °C) δ 0.86 [d, 6 H, $^2J(PtH)$ = 65, $^3J(AgH)$ = 4 Hz, *Me*Pt], 7.6–8.6 (m, 8 H, bpy); ^{195}Pt (−80 °C), δ 439 (s, v br, Pt).

Methyl Scrambling Reactions. Two solutions, each containing $[PtMe_2(bpy)]$ (5.4 mg) and $[Pt(CD_3)_2(bpy)]$ (5.4 mg) in CH_2Cl_2 (10 mL), were prepared. To one solution was added $AgBF_4$ (1.0 mg) in acetone (2 mL) at −78 °C, and the mixture was stirred for 5 min at −78 °C. A solution of NaCl in acetone was added, leading to precipitation of AgCl. The solution was warmed to room temperature, evaporated to dryness, and extracted with CH_2Cl_2 (10 mL) and the CH_2Cl_2 removed to give the product, shown by MS to contain $[PtMe_2(bpy)]$, $[PtMe(CD_3)(bpy)]$, and $[Pt(CD_3)_2(bpy)]$ (see text). The second solution, without $AgBF_4$, was treated in the same way to serve as a reference.

A solution containing $[Pt(CD_3)_2(bpy)]$ (2.7 mg) and $[PtMe_2(1,10\text{-phenanthroline})]$ (2.6 mg) in acetone-d_6 was prepared. After 2 h the ^1H NMR spectrum gave δ 1.11 [s, $^2J(PtH)$ = 85 Hz] due to $[PtMe_2(phen)]$ but no resonance at δ 0.95 due to $[PtMe_2(bpy)]$. Next, $AgBF_4$ (15 μL, 4×10^{-2} M in acetone) was added, and the NMR spectrum was recorded immediately. A resonance due to CH_3 groups of $[PtMe_2(bpy)]$ was observed at δ 0.95 [s, $^2J(PtH)$ = 86 Hz], demonstrating methyl for CD_3 scrambling. The experiment shows only the presence of CH_3Pt groups and does not distinguish between $[PtMe_2(bpy)]$ and $[PtMe(CD_3)(bpy)]$.

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Registry No. 1, 52594-52-2; **3a**, 115828-94-9; **3b**, 115936-51-1; **3c**, 115936-52-2; **3d**, 115828-96-1; 4, 115828-98-3; $[Au(NO_3)(PPh_3)]$, 14897-32-6; $[Au(BF_4)(PPh_3)]$, 67215-70-7; $Au(PF_6)PPh_3$, 83214-85-1; $AgPF_6$, 26042-63-7; $[AuCl(PPh_3)]$, 14243-64-2; $AgBF_4$, 14104-20-2; *fac*-$[PtMe_3(PPh_3)(bpy)]^+$, 47756-86-5; $[AuCl(SMe_2)]$, 29892-37-3; $[PtClMe_3(bpy)]$, 38194-03-5; $[PtClMe(bpy)]$, 50726-77-7; $[PtMe_2Cl(CH_2Cl)(bpy)]$, 115936-53-3; $[PtMe_2Cl_2(bpy)]$, 64507-94-4; $[Pt(CD_3)_2(bpy)]$, 115828-99-4; $[PtMe(CD_3)(bpy)]$, 115829-00-0; $[PtMe_2(1,10\text{-phenanthroline})]$, 52594-55-5; Au, 7440-57-5; Ag, 7440-22-4; Pt, 7440-06-4; $[Au(PPh_3)_2]NO_3$, 14853-96-4.

Gas-Phase Chemistry of First-Row Transition-Metal- and Metal-Containing Ions with Alkyl Cyanides

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The gas-phase ion/molecule reactions of first-row transition-metal ions with a series of alkyl cyanides is discussed, with the focus on the chemistry of Co^+. As the length of the alkyl chain of the nitrile increases, cleavage of C–C bonds far from the functional group is observed, which supports an initial "end-on" interaction with the –CN group. When a single ligand is attached to the metal, the resulting chemistry appears to be very different from that observed for the bare metal ion. The steric nature of the ligand effects is discussed. The observed ion/molecule reactions yield similar results to those suggested by collisional activation studies of transition-metal ion/alkyl cyanide complexes.

I. Introduction

For almost 15 years, reports have appeared in the literature concerning the rich chemistry that transition-metal ions exhibit with organic molecules in the gas phase.[1] Such studies are begining to provide fundamental insights into the structure/function relationships of organometallic chemistry. For the prototypical reaction[2]

$$Co^+ + C_3H_7Cl \rightarrow CoC_3H_6^+ + HCl \qquad (1)$$

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