Reactions of [MCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] (M = Pd or Pt) with [Rh$_2$(μ-Cl)$_2$(CO)$_4$]. Preparation of a Ph$_2$PCH$_2$SCH$_3$-bridged palladium-rhodium complex

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(Received November 7th, 1988)

Abstract

When *cis*-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] and [Rh$_2$(μ-Cl)$_2$(CO)$_4$] are allowed to react at ambient temperature *cis*-[PtCl$_2$(CO)(Ph$_2$PCH$_2$SCH$_3$)] and [Rh$_2$Cl$_2$(CO)$_2$(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$] are formed. By performing the reaction at −50°C the intermediate [PtCl(Ph$_2$PCH$_2$SCH$_3$)$_2$][RhCl$_2$(CO)$_2$] may be identified. In contrast [PdCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] reacts with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] to yield the mixed metal complex [PdRhCl$_3$(CO)(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$].

Introduction

There has been interest recently in the use of unsymmetrical, bidentate ligands analogous to bis(diphenylphosphino)methane (dppm) in forming mixed metal complexes. Balch, for example, has used 2-(diphenylphosphino)pyridine (Ph$_2$Ppy) and (diphenylarsino)(diphenylphosphino)methane (dapm) to generate Pd–Pt and Rh–Pt dimers [1]. In particular, he has shown that *cis*-[PtCl$_2$(Ph$_2$Ppy)$_2$] reacts with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] to give [PtCl(Ph$_2$Ppy)$_2$][RhCl$_2$(CO)$_2$] which, on heating, is converted to the ligand-bridged complex, [PtRhCl$_3$(CO)(μ-Ph$_2$Ppy)$_2$] [2].

We have shown previously that the reaction of *cis*-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] does not produce a mixed metal complex, but instead gives *cis*-[PtCl$_2$(CO)(Ph$_2$PCH$_2$SCH$_3$)] and the dimeric rhodium species [Rh$_2$Cl$_2$(CO)$_2$(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$] [3]. In this paper we describe studies on the mechanism of this reaction, and the successful formation of the analogous Pd–Rh complex, [PdRhCl$_3$(CO)(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$].

Results and discussion

When *cis*-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] and [Rh$_2$(μ-Cl)$_2$(CO)$_4$] are allowed to react together in CDCl$_3$ solution at ambient temperature a ligand exchange reaction

occurs according to eq. 1. No other products are observed. However, when the

$$2 \text{ } cis\text{-}[PtCl_2(Ph_2PCH_2SCH_3)_2] + [Rh_2(\mu\text{-}Cl)_2(CO)_4] \longrightarrow$$

$$2 \text{ } cis\text{-}[PtCl_2(CO)(Ph_2PCH_2SCH_3)] + [Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2] \quad (1)$$

reaction is performed at $-50\,^{\circ}C$ an intermediate is detected; in addition to some unreacted starting platinum complex the $^{31}P\{^{1}H\}$ NMR spectrum exhibits resonances due to the $[PtCl(Ph_2PCH_2SCH_3)_2]^+$ cation [3]. Attempts to isolate this intermediate in analytically pure form have not met with success, but removal of the solvent at $-30\,^{\circ}C$ followed by washing with ether gives a yellow solid. The $^{31}P\{^{1}H\}$ NMR spectrum of this material indicates that it contains $[PtCl(Ph_2PCH_2SCH_3)_2]^+$ and $cis\text{-}[PtCl_2(Ph_2PCH_2SCH_3)_2]$, but its infrared spectrum reveals the presence of the $[RhCl_2(CO)_2]^-$ anion ($\nu(CO)$ 1980 and 2060 cm^{-1}) [4]. When a solution of $[PtCl(Ph_2PCH_2SCH_3)_2][RhCl_2(CO)_2]$ is allowed to warm to ambient temperature a clean conversion to $cis\text{-}[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$ and $[Rh_2Cl_2(CO)_2\text{-}(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ takes place.

The first step in the reaction thus involves abstraction of chloride from platinum by $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$; abstraction of chloride by $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ has been observed previously [2,5]. The subsequent steps are somewhat unusual, however, since the end result is that the chloride is returned to platinum. Although we have not elucidated how these steps occur, we have made a number of observations that provide clues about the reaction mechanism.

When a solution of $[PtCl(Ph_2PCH_2SCH_3)_2][RhCl_2(CO)_2]$, generated at $-50\,^{\circ}C$, is allowed to warm to room temperature conversion to products is complete within about one hour. If carbon monoxide is passed through the solution as it is warmed the solution darkens much more quickly, and product formation is complete within 5 minutes. Thus the rate of the reaction is enhanced by the presence of the free ligand. If argon is bubbled through the solution as it is warmed, however, the expected products are not formed and the $^{31}P\{^{1}H\}$ NMR spectrum indicates the presence of a large number of unidentified species; extensive decomposition also takes place. This observation indicates that free carbon monoxide is generated during the course of the rearrangement.

In order to gain some insight into the CO transfer from rhodium to platinum we investigated the reaction of the $[PtCl(Ph_2PCH_2SCH_3)_2]^+$ cation with carbon monoxide. Treatment of $cis\text{-}[PtCl_2(Ph_2PCH_2SCH_3)_2]$ with 1 mol equiv. of $AgSO_3CF_3$ in CH_2Cl_2 solution allowed isolation, after removal of AgCl by filtration, of $[PtCl(Ph_2PCH_2SCH_3)_2]SO_3CF_3$. Its $^{31}P\{^{1}H\}$ NMR spectrum consists of two singlets, each with ^{195}Pt satellites; the high field signal is typical of a chelated four-membered ring [6]. The ^{1}H and ^{13}C signals for the methyl and methylene groups in the chelated ligand are shifted downfield significantly relative to those for the non-chelated ligand or the ligands in $cis\text{-}[PtCl_2(Ph_2PCH_2SCH_3)_2]$. The CH_2 hydrogens in the chelated ligand are magnetically non-equivalent, and exhibit a $^2J(HH)$ coupling constant of 15.2 Hz.

When a $CDCl_3$ solution of $[PtCl(Ph_2PCH_2SCH_3)_2]SO_3CF_3$ is treated with ^{13}CO and allowed to stand for 3 days at ambient temperature its $^{13}C\{^{1}H\}$ NMR spectrum contains a triplet resonance at 159.1 ppm, which is due to a terminal carbonyl. Its $^1J(PtC)$ value of 1813 Hz is indicative of CO lying *trans* to a ligand of low *trans*-influence such as chloride [7]. The $^{31}P\{^{1}H\}$ NMR spectrum contains a doublet ($^2J(PC)$ 8.5 Hz) whose $^1J(PtP)$ value is typical of a complex of the type *trans*-[PtCl-

$cis\text{-}[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2] + 0.5[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$
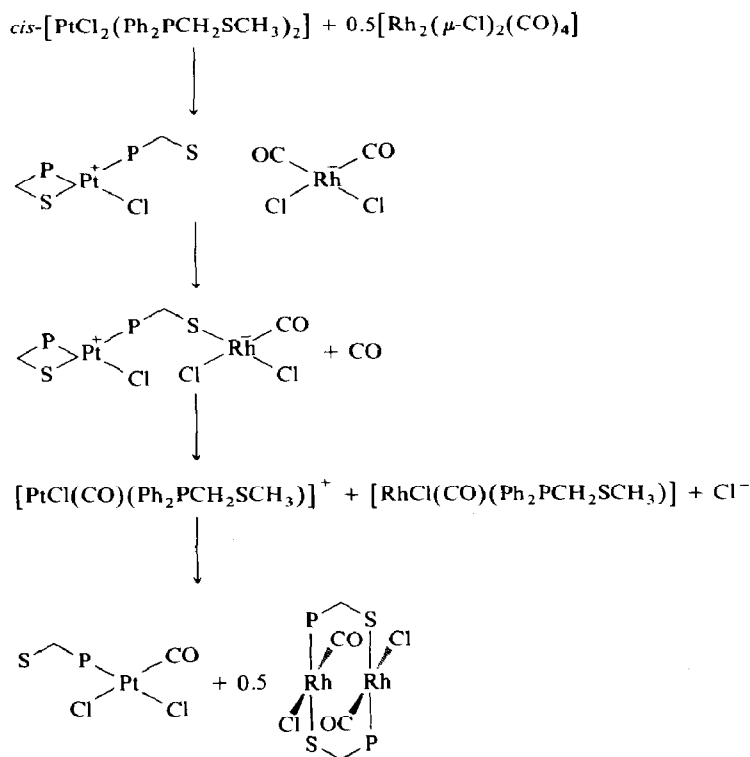
Scheme 1

$(\text{CO})(\text{PR}_3)_2]^+$ [8]. The product is thus identified as $trans\text{-}[\text{PtCl}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{-}\\\text{SCH}_3)_2]\text{SO}_3\text{CF}_3$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also reveals, however, that the reaction has proceeded only to the extent of about 20%; indeed, bubbling carbon monoxide through the solution for a total of 24 h results in only 50% conversion to the product.

Thus, the reaction of $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]^+$ with carbon monoxide alone is extremely slow, and it is clear that a simple dissociation of CO from $[\text{RhCl}_2(\text{CO})_2]^-$ followed by attack on the platinum cation cannot account for the rate of reaction of these two ions to give $cis\text{-}[\text{PtCl}_2(\text{CO})(\text{Ph}_2\text{PCH}_2\text{SCH}_3)]$ and $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-}\\\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]$. It is likely, however, that CO is displaced from $[\text{RhCl}_2(\text{CO})_2]^-$ by the free methylthio function of the $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]^+$ cation (Scheme 1), and the released carbon monoxide then coordinates to platinum. It is possible that when the $\text{Ph}_2\text{PCH}_2\text{SCH}_3$ ligand is bridging between the two metal centers, the cationic platinum center is more susceptible to attack by CO than $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]^+$ itself, or it may be that the ligand dissociates from platinum completely prior to attack by CO (the latter would be consistent with the observed decomposition in the absence of carbon monoxide). Transfer of one $\text{Ph}_2\text{PCH}_2\text{SCH}_3$ ligand from platinum to rhodium, followed by chloride transfer in the reverse direction and dimerization of the rhodium complex, would lead to the observed products.

In contrast to the reaction of $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]$, treatment of $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]$ with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$ in CH_2Cl_2 solution cleanly pro-

duces the mixed metal complex [PdRhCl$_3$(CO)(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$]. In CDCl$_3$ solution [PdCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] exists as a mixture of *cis* and *trans* isomers, the *trans* isomer being favored by a ratio of 3/1 at ambient temperature. On cooling to -50°C, however, the *cis* isomer is the major component (ca. 2/1 as evidenced by ^{31}P{^{1}H} NMR spectroscopy). When [Rh$_2$(μ-Cl)$_2$(CO)$_4$] is added to a CDCl$_3$ solution of [PdCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] at -50°C no reaction takes place, but on warming to -30°C slow formation of the mixed metal complex occurs. No intermediate species are observed. Raising the temperature to 20°C results in complete conversion to [PdRhCl$_3$(CO)(μ-Ph$_2$PCH$_2$SCH$_3$)$_2$] within a few minutes.The product is assigned the structure **1** on the basis of its NMR parameters [9].

(1)
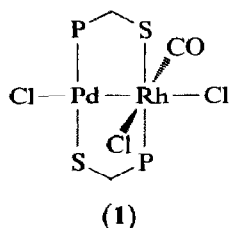
Its ^{31}P{^{1}H} NMR spectrum consists of a doublet for the P atom coordinated to palladium and a doublet of doublets for the P atom attached to rhodium, indicating that it exists in solution as the "head-to-tail" isomer only. Since no intermediates are detected, even at the lowest temperature at which the reaction proceeds, it is unclear whether the first step in the reaction sequence is analogous to that found with platinum.

Experimental

All reactions were carried out under argon, unless otherwise stated. Ph$_2$PCH$_2$SCH$_3$ was prepared as described previously [4]. The complexes [Rh$_2$(μ-Cl)$_2$(CO)$_4$] and *cis*-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] were prepared by established procedures [4,10]. Carbon-13 monoxide (99% enriched) was purchased from Aldrich. Microanalyses were performed by Atlantic Microlab Inc., Norcross, Georgia or Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded for CDCl$_3$ solutions on a Varian XL-300 spectrometer at 300.0, 75.4 and 121.4 MHz respectively. Chemical shifts are reported in ppm relative to TMS or external 85% H$_3$PO$_4$, positive shifts representing deshielding. Infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer.

NMR characterization of cis-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$]
^{1}H NMR: δ 1.89 CH_3; 3.57 (d, ^2J(PH) 6.5 Hz, J(PtH) unresolved) CH_2; 7.2, 7.4, 7.6 (m); ^{13}C{^{1}H} NMR: δ 18.63 (t, J(PC) 2.0 Hz) CH_3; 34.06 (d, J(PC) 40.5 Hz) CH_2; 128.08 (t), 131.32, 133.86 (t);^{31}P{^{1}H} NMR: δ 7.37, ^1J(PtP) 3679 Hz.

Preparation of [PdCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$]
Ph$_2$PCH$_2$SCH$_3$ (1.39 g, 5.65 mmol) was dissolved in CH$_2$Cl$_2$ (50 ml). Palladium(II) chloride (0.500 g, 2.82 mmol) was added, followed by a further 30 ml

of CH_2Cl_2. After stirring overnight the yellow solution was filtered to remove unreacted $PdCl_2$ then reduced in volume, and ether was added to precipitate the product as yellow crystals (1.51 g, 80%). ^1H NMR: δ 1.82 (*trans* isomer), 1.91 (*cis*) CH_3; 3.64 (*trans*), 3.70 (d, ^2J(PH) 5.1 Hz, *cis*) CH_2; $^{31}P\{^1H\}$ NMR: δ 17.4 (*trans*), 28.1 (*cis*). Found: C, 50.30; H, 4.38. $C_{28}H_{30}Cl_2P_2PdS_2$ calcd.: C, 50.20; H, 4.51%.

Preparation of [PdRhCl₃(CO)(μ-Ph₂PCH₂SCH₃)₂]

[PdCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] (0.101 g, 0.151 mmol) was dissolved in CH_2Cl_2 (3 ml), then [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (0.030 g, 0.077 mmol) was added. After 1 h ether was added and the solution was kept at $-30°C$ overnight. An orange solid was separated by filtration (0.093 g, 74%), and recyrstallization from CH_2Cl_2/Et_2O gave the product as dark red crystals, ν(CO) 2020 cm^{-1} (Nujol mull). ^1H NMR: δ 2.71 (d, ^4J(PH) 3.2 Hz), 2.81 (d, ^4J(PH) 4.5 Hz) CH_3; four multiplets centered at 3.9, 4.1, 4.5, 4.8 due to CH_2 groups; $^{13}C\{^1H\}$ NMR: δ 21.0 (d, ^3J(PC) 9.2 Hz), 23.6 (d, ^3J(PC) 6.9 Hz) CH_3; 40.9 (d, ^1J(PC) 29.8 Hz), 42.4 (d, ^1J(PC) 26.6 Hz) CH_2; $^{31}P\{^1H\}$ NMR: δ 17.9 (d, ^3J(PP) 14.6 Hz), 26.2 (dd, ^1J(RhP) 110.6 Hz, ^3J(PP) 14.6 Hz). Found: C, 41.38; H, 3.66. $C_{29}H_{30}Cl_3OP_2PdRhS_2$ calcd.: C, 41.65; H, 3.62%.

Preparation of [PtCl(Ph₂PCH₂SCH₃)₂]SO₃CF₃

cis-[PtCl$_2$(Ph$_2$PCH$_2$SCH$_3$)$_2$] (0.127 g, 0.167 mmol) was dissolved in CH_2Cl_2 (8 ml), then AgSO$_3$CF$_3$ (0.043 g, 0.167 mmol) was added and the mixture was stirred for 1 h. After filtration the solvent was removed, and the oily residue was dissolved in CH_3OH/Et_2O. Cooling to $-30°C$ gave the product as pale yellow crystals (0.113 g, 77%), which were dried in vacuo. ^1H NMR: δ 2.04 (d, ^4J(PH) 1.0 Hz), 2.95 (d, ^4J(PH) 4.9 Hz, ^3J(PtH) unresolved) CH_3; 3.62 (dd, J(PH) 7.0, 4.6 Hz, 2H), 5.24 (dd, ^2J(HH) 15.2 Hz, ^2J(PH) 6.5 Hz, 1H), 5.51 (dd, ^2J(HH) 15.2 Hz, ^2J(PH) 8.6 Hz, 1H) CH_2. $^{13}C\{^1H\}$ NMR: δ 19.0 (d, ^3J(PC) 4.7 Hz), 23.3 (s) CH_3; 30.9 (d, ^1J(PC) 36.1 Hz), 49.5 (dd, ^1J(PC) 41.3 Hz, ^3J(PC) 2.2 Hz) CH_2; $^{31}P\{^1H\}$ NMR δ 9.4, ^1J(PtP) 3281 Hz; -58.7, ^1J(PtP) 3039 Hz. Found: C, 39.97; H, 3.52. $C_{29}H_{30}ClF_3O_3P_2PtS_3$ calcd.: C, 39.93; H, 3.47%.

Reaction of [PtCl(Ph₂PCH₂SCH₃)₂]SO₃CF₃ with carbon monoxide

A CDCl$_3$ solution of [PtCl(Ph$_2$PCH$_2$SCH$_3$)$_2$]SO$_3$CF$_3$ (20 mg) was placed in a 5-mm NMR tube fitted with a rubber septum cap. The tube was evacuated, then filled with ^{13}CO. After 3 days spectroscopic examination revealed that 20% reaction had occurred to give *trans*-[PtCl(^{13}CO)(Ph$_2$PCH$_2$SCH$_3$)$_2$]SO$_3$CF$_3$. $^{13}C\{^1H\}$ NMR: δ 159.1 (t, ^2J(PC) 8.5 Hz, ^1J(PtC) 1813 Hz); $^{31}P\{^1H\}$ NMR: δ 19.3 (d, ^2J(PC) 8.5 Hz, ^1J(PtP) 2025 Hz). Passing a stream of CO through the solution for 16 h resulted in 50% conversion to *trans*-[PtCl(CO)(Ph$_2$PCH$_2$SCH$_3$)$_2$]SO$_3$CF$_3$. Slow loss of CO, and regeneration of [PtCl(Ph$_2$PCH$_2$SCH$_3$)$_2$]SO$_3$CF$_3$, occurred on standing at ambient temperature.

Acknowledgements

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