shows a weak signal of ≈+1 mdeg at 552 nm due to the Δ isomer, which indicates preferential binding to the protein by the Λ isomer. The experiment is difficult and the magnitude of the result is at the limits of detection; however, a similar result was obtained that indicated the selective binding of Λ-$[Co(ox)_3]^{3-}$ to the oxidized protein in a previous study.[15] Like the stereoselective electron-transfer experiment, interpretation of this chiral recognition of $[Cr(ox)_3]^{3-}$ by cytochrome *c* is difficult. Although the number of strong interactions between the protein and $[Cr(ox)_3]^{3-}$ appears limited, the stereoselectivity observed is the weighted average of all the interactions that take place. Thus, a highly stereoselective but minor interaction can make a larger contribution to the overall value than a dominant, less selective interaction. Nevertheless, it is of considerable interest to note that the chiral recognition in the binding interaction favors the same Λ isomer as chiral induction in the electron-transfer process.

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Registry No. $[Co(ox)_3]^{3-}$, 15053-34-6; Λ-$[Co(ox)_3]^{3-}$, 21826-66-4; Δ-$[Co(ox)_3]^{3-}$, 82409-68-5; cytochrome *c*, 9007-43-6.

Contribution from the Laboratorium für Anorganische
Chemie, Eidgenössische Technische Hochschule,
CH-8092 Zürich, Switzerland

A Simple Synthetic Route to Platinum–Carbonyl–Phosphine Cluster Compounds

Klaus-Hermann Dahmen,* Alfred Moor, Ralph Naegeli,
and Luigi M. Venanzi

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Introduction

Transition-metal carbonyl cluster compounds have been extensively studied over the last 30 years.[1] Many of these compounds homogeneously catalyze reactions such as the hydrogenation of carbon monoxide[2] and alkenes[3] or the water gas shift reaction.[4] Of particular interest has also been the analogy between transition-metal surfaces employed in heterogeneous catalysis and cluster compounds.[5] Platinum clusters of the type $[Pt_3(\mu_2\text{-}CO)_3L_3]$ (L = bulky tertiary phosphine) (3:3:3; **1**) have also been employed as starting materials for the synthesis of heterometallic cationic species of the types $[\{Hg_2\}(3{:}3{:}3)_2]^+$,[6] $[\{LM\}(3{:}3{:}3)]^+$,[7] and $[M(3{:}3{:}3)_2]^+$[8] (L = PR_3; M = Cu, Ag, Au).

However, the application of compounds of type **1** in both homogeneous and heterogeneous catalysis has hardly been investigated to date. This may be related to the lack of availability of a systematic methodology for preparing these compounds as well as their homologues $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (4:5:4; **2**). Furthermore, established methods require the use of compounds such as $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene),[9] which is not easily accessible, or of the type *trans*-$[PtHCl(PR_3)_2]$.[10] Here we report a simple preparative method for compounds of types **1** and **2**.

Experimental Section

Solvents were obtained from Fluka and used as received. Other reagents employed: $NaBH_4$, Fluka purum; $PtCl_2$, Johnson Matthey; PMe_2Ph, Fluka purum. The other ligands $P(^iPr)_3$,[11] and $PPh(^iPr)_2$,[12] $PPhCy_2$,[13] PCy_3,[14] and $PMeCy_2$[15] and the intermediates $[PtCl_2(MeCN)_2]$ (**3**)[16] and $[PtCl_2(COD)]$ (**4**)[17] were prepared by literature methods. The IR spectra were recorded on a Perkin-Elmer 1430 spectrometer, and the NMR spectra were obtained on a Bruker HX 90, WH 90, or WM 250 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the ETH, Zürich.

Synthesis of the Compounds $[Pt_3(\mu_2\text{-}CO)_3L_3]$ and $[Pt_4(\mu_2\text{-}CO)_5L_4]$. General Procedure. The complex $[PtCl_2(MeCN)_2]$ (or $[PtCl_2(COD)]$) (0.2–1 g) was suspended in acetonitrile (10–50 mL). The tertiary phosphine (1 equiv) was added, and the resulting clear solution (or suspension) was stirred for 30 min while carbon monoxide was bubbled through the solution. On addition of an excess of solid $Na[BH_4]$ (ca. 5 equiv), the mixture slowly turned brown. After 20 min of stirring under a carbon monoxide atmosphere, 2–5 mL of CH_3OH was slowly added. Increased gas evolution was observed, and the mixture turned red. Stirring under a carbon monoxide atmosphere was continued for 3 h. The solvent was then removed under vacuum, and the brown residue was extracted with dichloromethane or toluene. The dark solution was filtered through Celite and concentrated under reduced pressure to a few milliliters. Addition of a large volume of CH_3OH (50–100 mL) gave, after cooling to −20 °C overnight, the product as a crystalline material. Unless otherwise noted, all compounds are air stable both in solid state and in solution.

$[Pt_3(\mu\text{-}CO)_3(P(^iPr)_3)_3]$ (1a): from **3** (1.1 g, 3.16 mmol) and P^iPr_3 (0.51 g, 3.16 mmol); yield 80%. Anal. Calcd for $C_{30}H_{63}O_3P_3Pt_3$: C, 31.34; H, 5.52. Found: C, 31.93; H, 5.50.

$[Pt_3(\mu_2\text{-}CO)_3(PPh^iPr_2)_3]$ (1b): from **3** (1 g, 2.87 mmol) and PPh^iPr_2 (0.6 g, 3.09 mmol); yield 80%. Anal. Calcd for $C_{39}H_{57}O_3P_3Pt_3$: C, 37.41; H, 4.59. Found: C, 37.54; H, 4.54.

$[Pt_3(\mu_2\text{-}CO)_3(PPhCy_2)_3]$ (1c): from **4** (0.6 g, 1.60 mmol) and $PPhCy_2$ (0.45 g, 1.64 mmol); yield 80%. Anal. Calcd for $C_{57}H_{81}O_3P_3Pt_3$: C, 45.27; H, 5.47. Found: C, 44.87; H, 5.42.

$[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ (1d): from **4** (1 g, 2.67 mmol) and PCy_3 (0.75 g, 2.67 mmol); yield 65%. Anal. Calcd for $C_{57}H_{99}O_3P_3Pt_3$: C, 45.32; H, 6.61. Found: C, 45.42; H, 6.71.

$[Pt_4(\mu_2\text{-}CO)_5(PBz_3)_4]$ (2a): from **4** (0.8 g, 2.14 mmol) and PBz_3 (0.65 g, 2.14 mmol); yield 65%. Anal. Calcd for $C_{89}H_{84}O_5P_4Pt_4$: C, 50.00; H, 3.40. Found: C, 49.89; H, 4.18.

$[Pt_4(\mu_2\text{-}CO)_5(PMe_2Ph)_4]$ (2b): from **3** (1 g, 2.87 mmol) and PMe_2Ph (0.4 g, 2.90 mmol); yield 70%. Anal. Calcd for $C_{37}H_{44}O_5P_4Pt_4$: C, 30.16; H, 2.99. Found: C, 30.35; H, 3.00.

$[Pt_4(\mu_2\text{-}CO)_5(PEt_3)_4]$ (2c): from **3** (0.8 g, 2.87 mmol) and PEt_3 (0.34 g, 2.87 mmol); yield 70%. Anal. Calcd for $C_{32}H_{42}O_5P_4Pt_4$: C, 25.00; H, 4.34. Found: C, 25.11; H, 4.19.

Results and Discussion

Preparation of the Compounds $[Pt_3(\mu\text{-}CO)_3L_3]$ (L = P^iPr_3 (1a), PPh^iPr_2 (1b), $PPhCy_2$ (1c), PCy_3 (1d)) and $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (L = PBz_3 (2a), PMe_2Ph (2b), PEt_3 (2c)). The preparation of compounds **1a–d** and **2b** starting from either *cis*-$[PtCl_2(PR_3)_2]$ or *trans*-$[PtHCl(PR_3)_2]$[10a] and using CO in alkaline solution as reducing agent has been previously reported. Goel and coworkers[10b] described the formation of $[PtH_2(PR_3)_2]$ starting from $[PtCl_2(COD)]$ and bulky phosphines. Reductive elimination of H_2, in the presence of CO, gave the $[Pt_3(\mu_2\text{-}CO)_3(PR_3)]$ clusters. We find that this rather cumbersome procedure can be avoided

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Table I. Dependence of Cluster Type Formation[a] on Phosphine Cone Angle θ

phosphine	cluster type[b] 4:5:4	3:3:3	3:3:4	θ, deg
PMe_2Ph	+		+	122
PEt_3	+		+	132
$PMePh_2$	+		+	136
PPh_3	(+)	(+)	+	145
$PEt_2{}^tBu$	+	+	+	148
$PPh_2{}^iPr$		+	+	150
$PPh{}^iPr_2$		+		152
$P{}^iPr_3$		+		154
$PPhCy_2$		+		160
PBz_3	+	+		161
PCy_3		+		170

[a] These clusters have also been prepared by a variety of other methods.[9b,19,20] [b] 3:3:3 = $[Pt_3(\mu_2\text{-}CO)_3(PR_3)_3]$; 4:5:4 = $[Pt_4(\mu_2\text{-}CO)_5(PR_3)_4]$; 3:3:4 = $[Pt_3(\mu_2\text{-}CO)_3(PR_3)_4]$. The clusters marked with + were isolated, characterized, and obtained analytically pure. Those marked (+) were only detected in solution by $^{31}P\{^1H\}$ NMR spectroscopy. The same technique showed no evidence for the formation of any of the other possible clusters.

and that compounds **1a–d** and **2a–c** can easily be obtained in good yields simply by adding 1 equiv of tertiary phosphine to a suspension of either $[PtCl_2(MeCN)_2]$ (**3**) or $[PtCl_2(COD)]$ (**4**) in acetonitrile, under 1 atm of carbon monoxide, and treating the resulting mixture with sodium borohydride. Since $[PtCl_2(MeCN)_2]$ is simply and quantitatively obtained by refluxing $PtCl_2$ in acetonitrile, this procedure represents a direct "one-pot" synthetic method with yields ranging from 60 to 90%, depending on the phosphine employed.

The bulky phosphines $P{}^iPr_3$, PCy_3, $PPh{}^iPr_2$, and $PPhCy_2$ form preferentially complexes of type **1**, while the less bulky phosphines PEt_3 and $PPhMe_2$ yield only clusters of the type **2**.

Problems were encountered when phosphines containing more than one aryl group, e.g., $PMePh_2$ or PPh_3, were employed. In these cases $^{31}P\{^1H\}$ NMR spectroscopy of the methylene chloride extracts showed the presence of mixtures of clusters of the types $[Pt_3(\mu_2\text{-}CO)_3L_3]$ (**1**; 3:3:3), $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (**2**; 4:5:4), and $[Pt_3(\mu_2\text{-}CO)_3L_4]$ (**5**; 3:3:4). Furthermore, it proved to be extremely difficult to prepare clusters of the type $[Pt_3(\mu_2\text{-}CO)_3L_4]$ (**5**) by this route.

The preferential formation of clusters of type **1**, **2**, or **5** depends largely (1) on the Pt:PR_3 ratio and (2) on the bulk of the phosphine. Using the method described above as well as other synthetic routes,[9,10] it has been possible to establish the dependence of the cluster type formed on the phosphine cone angle, θ.[18] The results are summarized in Table I. When the Pt:P ratio is 1, only complexes of the types **1** and **2** are formed. As can be seen there, phosphines with θ of 136° or below form only clusters of type **2**, while phosphines of cone angle of 152° and above form only compounds of type **1**, with the exception of PBz_3, which has been assigned a θ value of 161°.[18] However, this anomaly may be explained by taking into account the great flexibility of these substituents, which, in part, can be folded up to give a ligand with θ of ca. 148°. It is also observed that for phosphines with θ between 145 and 150° both types of compounds coexist in solution.

Analogous studies carried out on solutions containing Pt:P ratios of 1:2, or larger, showed that clusters of type **5** were formed if the phosphine cone angle does not exceed 150°. Also, in these cases, clusters of different type can coexist in solution. However, as they are in equilibrium, in general one can only isolate the least soluble compound.

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Contribution from Sterling Chemistry Laboratory,
Department of Chemistry, Yale University,
New Haven, Connecticut 06511-8118

Synthesis and Characterization of Rhenium Complexes with 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($P(OCH_2)_3CEt$)

Xiao-Liang Luo,* Demetrius Michos, and Robert H. Crabtree*

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Introduction

The chemistry of rhenium phosphite complexes is relatively unexplored as compared to that of the phosphine analogues. Only a few reports on rhenium phosphites have appeared in the literature.[1] In particular, little work has been done on rhenium phosphite polyhydride complexes. This is surprising because a wide range of the corresponding phosphine complexes are known. Such complexes can have unusual structures and reactivity patterns.[2] For example, protonation of $ReH_3(CO)(PMe_2Ph)_3$ gives an equilibrium mixture of a classical eight-coordinate tetrahydride $[ReH_4(CO)(PMe_2Ph)_3]^+$ and its nonclassical seven-coordinate dihydrogen dihydride tautomer $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$,[3] and $ReH_7(PPh_3)_2$ is an efficient catalyst for C–H bond activation.[4]

As ligands, phosphites are generally more electron-withdrawing and sterically less bulky than phosphines.[5] Replacement of phosphines in a polyhydride complex by phosphites may have interesting effects on both structure and reactivity as a result of different electronic and steric properties. For example, the electron-withdrawing character of phosphite ligands may favor nonclassical structures with one or more η^2-H_2 ligands by reducing the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation.

Very few phosphite-supported polyhydrides are known, probably because phosphite ligands do not usually tolerate strongly reducing hydridometalates such as $LiAlH_4$ and $NaBH_4$, which are often used in the preparation of polyhydrides from their halide precursors. For example, an attempted preparation of $ReH_5\{P(OMe)_3\}_3$ by treatment of $ReCl_3\{P(OMe)_3\}_3$ with various hydridometalates led to an intractable product.[1h]

In a brief communication, Caulton et al. reported the first examples of high-oxidation-state rhenium phosphite polyhydrides, $ReH_5\{P(OEt)_3\}_3$ and $ReH_7\{P(OEt)_3\}_2$.[1g] We looked at the coordination chemistry of rhenium with the cyclic phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($P(OCH_2)_3CEt$, ETPB) in the hope that the special cage structure of the ligand might make it more resistant to hydridometalates in the preparation of polyhydrides. In this paper we describe the synthesis and characterization of several new rhenium complexes with ETPB, including two rare rhenium phosphite polyhydrides.

Results

The synthetic routes to the rhenium ETPB complexes, starting from $ReOCl_3(PPh_3)_2$, are summarized in Scheme I. The new complexes were identified by microanalysis and spectroscopic studies, including T_1 data. These are presented in the Experimental Section and in Table I.

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