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ASPECTS OF ANIONIC RHODIUM COMPLEXES. LIGAND EFFECTS *

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Summary

As an aid to the understanding of the mechanistic details of the rhodium-catalyzed hydroformylation of formaldehyde, a proposed active catalyst, $[Rh(CO)_3(PPh_3)]^-$, was synthesized and characterized. Other anionic rhodium complexes such as $[Rh(CO)_3(PPh_2Me)]^-$, $[Rh(CO)_3(PPhMe_2)]^-$, $[Rh(CO)_3(PMe_3)]^-$, $[Rh(CO)_2(Diphos)]^-$, and $[Rh(CO)_2(P(OPh)_3)_2]^-$, were also synthesized and studied. The molecular structure of $[Rh(CO)_3(PPh_3)]^-$, $[Rh(CO)_2(Diphos)]^-$, and $[Rh(CO)_2(P(OPh_3)_2]^-$ were determined by single crystal X-ray diffraction studies. The chemistry involved in the syntheses of these complexes and the ligand effects related to them are discussed.

Introduction

Anionic rhodium complexes have been an interesting subject in the fields of organometallic chemistry and homogeneous catalysis [1–5]. In our recent studies on the hydroformylation of formaldehyde, we found that the reaction rates could be increased by adding a Lewis base to the catalyst system; rate enhancements were particularly noticeable when high phosphine-to-rhodium ratios were used. A mechanism involving an anionic tricarbonyl(triphenylphosphine)rhodate(−1) catalyst was proposed [2].

In order to explore the mechanistic details of this catalytic reaction, we felt that it was important for us to synthesize and characterize several rhodium anions and use them as models for our in situ infrared spectroscopic study.

Although the synthesis of anionic rhodium complexes containing both carbonyl and phosphine ligands has been claimed before, none of these compounds have been isolated and definitively characterized [3–5]. There has been some controversy over the nature of the species in solution. Collman et al. reported that the reduction of

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* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

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$RhCl(CO)(PPh_3)_2$ by sodium amalgam in tetrahydrofuran (THF) under a CO atmosphere generated $[Rh(CO)_2(PPh_3)_2]^-$. This anion was not isolated but its formation was inferred from the formation of $Me_3SnRh(CO)_2(PPh_3)_2$ when trimethyltin chloride was added to the solution [3]. Haszeldine et al. suggested that the same Rh anion could be obtained by reducing $Rh_2(CO)_4(PPh_3)_4$ [6] with sodium amalgam at room temperature under atmospheric pressure of CO [4]. The infrared absorptions for the carbonyls were reported to be at 1880 and 1850 cm^{-1}. Recently Zotti, Zecchin, and Pilloni reported that $[Rh(CO)_2(PPh_3)_2]^-$ was obtained by electrochemically reducing $[Rh(CO)(PPh_3)_3]^+$ followed by reaction with CO. The infrared stretching frequencies for the carbonyls were reported to be 1855 and 1805 cm^{-1} [5]. In order to elucidate the nature of these and related rhodium anions, we undertook a careful study of these complexes and report our results here.

Results and discussion

When we repeated Collman's reaction and followed the reaction using high pressure infrared spectroscopy, it was found that under the reaction conditions (60 psi CO), only one metal carbonyl absorption at 1900 cm^{-1} was observed. A ^{31}P NMR study of the solution under 60 psi CO showed only free triphenylphosphine. These results indicate that under those conditions $[Rh(CO)_4]^-$ [8] was the reaction product.

$$RhCl(CO)(PPh_3)_2 \xrightarrow[THF]{Na-Hg,CO} [Rh(CO)_4]^- + 2PPh_3 + NaCl\downarrow$$

The formation of $[Rh(CO)_4]^-$ rather than $[Rh(CO)_2(PPh_3)_2]^-$ is certainly caused by the electronic effect of the metal–ligand interactions. Although phosphines are good ligands for cationic and neutral Rh complexes, the anionic species prefer more electron withdrawing ligands such as CO to dissipate the negative charge. When the solution was filtered under vacuum, one of the carbonyl ligands was slowly replaced by a triphenylphosphine molecule and $[Rh(CO)_3(PPh_3)]^-$ was formed. (ν(CO) 1931s, 1858vs cm^{-1}). The carbonyl stretching frequencies of these complexes are identical to those observed in the in situ high pressure infrared spectroscopic study of formaldehyde hydroformylation [2], and thus confirm our belief that these anions are important catalytic agents in the Rh-catalyzed hydroformylation of formaldehyde.

When a slight excess of 18-crown-6 ether was added to a THF solution of $Na[Rh(CO)_3(PPh_3)]$ followed by the addition of a large excess of diethyl ether, a yellow powder of crown ether complexed sodium tricarbonyl(triphenylphosphine)rhodate(−1) was isolated in high yield (> 90%). The slow addition of diethyl ether yielded crystals of this complex. The yellow complex is extremely air-sensitive and turns black immediately upon exposure to air. A single crystal X-ray diffraction study of this material revealed a slightly distorted tetrahedral structure for the anionic moiety. The sodium cation, which is complexed by the crown ether, is bound to the anion through the oxygen atom of one of the carbonyl ligands. The 18-crown-6 ether is highly puckered to allow all the oxygen atoms to bind to the small sodium cation. A perspective view of the structure of this complex is illustrated in Fig. 1.

Other monodentate phosphine ligands for the rhodium anion

Once the structure of $[Rh(CO)_3(PPh_3)]^-$ was characterized, it was of interest to study the electronic and steric effect of other monodentate phosphine ligands on the rhodium anion. For convenience of comparison, methyldiphenylphosphine, dimethylphenylphosphine and trimethylphosphine were used.

The anionic complexes, $[Rh(CO)_3L]^-$ (where L = PPh_2Me, $PPhMe_2$, PMe_3), were prepared either by reducing the corresponding chlorocarbonylbisphosphine species, $RhCl(CO)L_2$, or by adding an excess of the corresponding phosphine into a THF solution of $[Rh(CO)_4]^-$ which was made by reducing $[Rh(CO)_2Cl]_2$ in THF under CO.

$$[Rh(CO)_2Cl]_2 \xrightarrow[\text{THF}]{\substack{\text{K-Hg or}\\ \text{Na-Hg,CO}}} [Rh(CO)_4]^- \xrightarrow[-\text{CO}]{\text{L}} [Rh(CO)_3L]^-$$

An interesting observation in this study is that for these rhodium anions the infrared stretching frequencies of the carbonyls are very similar even though the phosphine ligands are very different in electronic and steric nature. Our infrared data for these anions in THF are summarized as the following: $K[Rh(CO)_3(PPh_2Me)]$: 1931s, 1862vs cm^{-1}; $K[Rh(CO)_3(PPhMe_2)]$: 1929s, 1858vs cm^{-1}; $K[Rh(CO)_3(PMe_3)]$: 1929s, 1858 vs cm^{-1}.

$Ph_2PCH_2CH_2PPh_2$ (Diphos) as a ligand

Since chelating phosphine ligands are well known to strongly coordinate to the metal center, it was of interest for us to examine the behavior of anionic rhodium complexes which contained a Diphos ligand.

When $Na[Rh(CO)_4]$ was allowed to react with one equivalent of Diphos in THF, $Na[Rh(CO)_3(Diphos^\star)]$ (Diphos★ = a monodentate, dangling Diphos) was found to

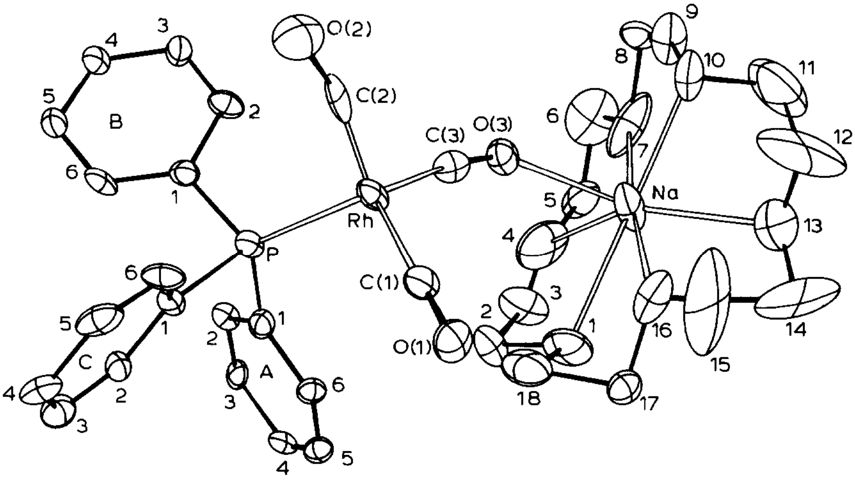

Fig. 1. A perspective view of $[Na(C_{12}H_{24}O_6)][Rh(CO)_3(PPh_3)]$. Principle bond lengths (Å): Rh–C(1), 1.877; Rh–C(2), 1.82; Rh–C(3), 1.87; Rh–P, 2.323; C(1)–O(1), 1.136; C(2)–O(2), 1.26; C(3)–O(3), 1.185; Na–O(3), 2.535. Principle bond angles (degrees): C(1)–Rh–C(2), 113.0; C(1)–Rh–C(3), 107.4; C(1)–Rh–P, 106.3; C(2)–Rh–C(3), 112.1; C(2)–Rh–P, 105.4; C(3)–Rh–P, 112.6; Rh–C(1)–O(1), 177; Rh–C(2)–O(2), 169; Rh–C(3)–O(3), 172; C(3)–O(3)–Na, 146.

be the first reaction product. (ν(CO) 1928, 1865 cm^{-1}) (^{31}P NMR in THF: δ(P(1)) (coordinated) 35.4 ppm, δ(P(2)) (dangling P) -14.9 ppm, J(Rh–P(1)) 150 Hz, J(P(1)–P(2)) 41.5 Hz.) The monodentate coordination mode of Diphos is a good indication for the strong coordination of CO in anionic complexes. When the solution was stirred under nitrogen atmosphere for several weeks Na[Rh(CO)$_2$(Diphos)] was obtained. (ν(CO) 1863, 1802 cm^{-1} [5].) When an excess of diethyl ether was slowly added to a THF solution of Na[Rh(CO)$_2$(Diphos)], single crystals of [Na(THF)$_2$][Rh(CO)$_2$(Diphos)] were obtained. An X-ray diffraction study of this complex revealed the expected, slightly distorted tetrahedral structure for the anion. The sodium cation, which is solvated by two THF molecules, ligates to the rhodium anion through one of the carbonyl ligands. A perspective view of this structure is shown in Fig. 2.

Use of triphenylphosphite as ligands

The formation of [Rh(CO)$_2$(Diphos)]$^-$ from the reaction of [Rh(CO)$_4$]$^-$ with Diphos indicated that the chelate effect of Diphos can promote the substitution of the second carbon monoxide ligand. Since an important factor for the carbonyl ligands in the anionic rhodium complexes is their π electron accepting nature, it was

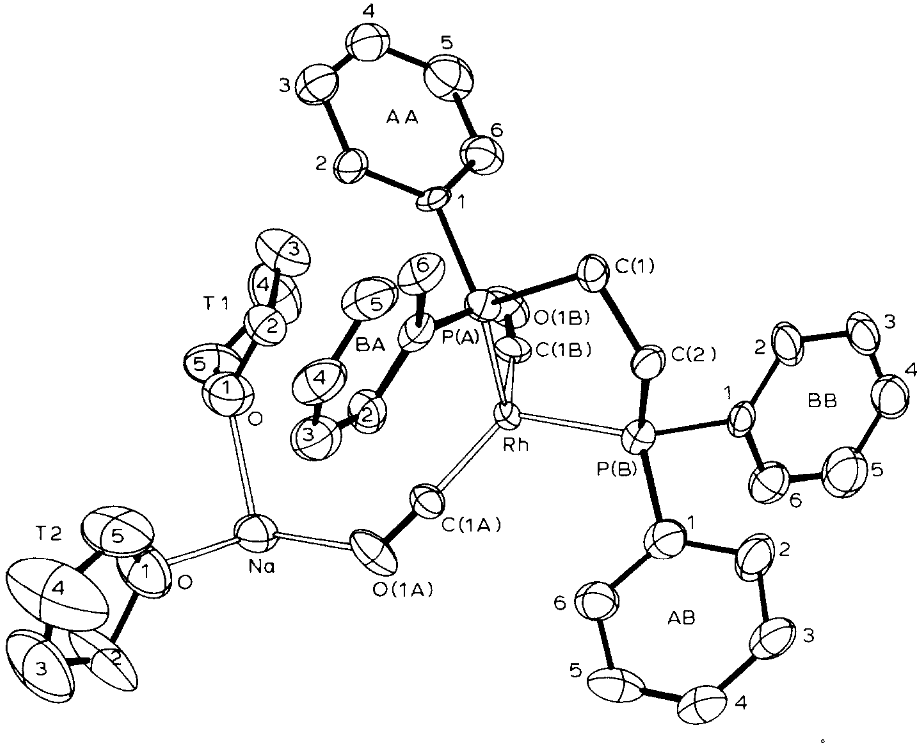

Fig. 2. A perspective view of [Na(THF)$_2$][Rh(CO)$_2$(Diphos)]. Principle bond lengths (Å): Rh–C(1A), 1.84; Rh–C(1B), 1.850; Rh–P(A), 2.306; Rh–P(B), 2.300; C(1A)–O(1A), 1.158; C(1B)–O(1B), 1.181; Na–O(1A), 2.408; Na–O(1T1) 2.303; Na–O(1T2), 2.283. Principle bond angles (degrees): C(1A)–Rh–C(1B), 116.6; C(1A)–Rh–P(A), 113.1; C1A–Rh–PB, 117.1; C(1B)–Rh–P(A), 102.6; C(1B)–Rh–P(B), 116.2; P(A)–Rh–P(B), 85.76; Rh–C(1A)–O(1A), 174.8; Rh–C1B–O1B, 171.6; C(1A)–O(1A)–Na, 121.2; O(1A)–Na–O(1T1), 106.8; O(1A)–Na–O(1T2), 98.1; O(1T1)–Na–O(1T2), 98.8.

conceivable that even in the absence of the chelate effect, $[Rh(CO)_2L_2]^-$ could still be prepared by reacting $[Rh(CO)_4]^-$ with π electron accepting ligands. When two equivalents of triphenylphosphite ligands were added to a THF solution of $[Rh(CO)_2Cl]_2$ and the final solution was subjected to reduction (potassium amalgam under a CO atmosphere), both $[Rh(CO)_4]^-$ and $[Rh(CO)_3(P(OPh)_3)]^-$ (ν(CO) 1962, 1860 cm^{-1}) were observed. After filtration under vacuum and allowing the solution to stir under a nitrogen atmosphere for several days, $[Rh(CO)_2(P(OPh)_3)_2]^-$ became the major species (ν(CO) 1933, 1881 cm^{-1}).

$$\begin{tikzcd}
{[Rh(CO)_2Cl]_2} \arrow[r, "K-Hg,CO", "THF"'] & {[Rh(CO)_4]^- + [Rh(CO)_3(P(OPh)_3)]^-} \arrow[d, shift left] \\
 & {[Rh(CO)_2(P(OPh)_3)_2]^-} \arrow[u, shift left, "-CO, + P(OPh)_3"']
\end{tikzcd}$$

When a slight excess of 18-crown-6 ether was added to a THF solution of $K[Rh(CO)_2(P(OPh)_3)_2]$, the potassium cation was complexed by the crown ether, and the addition of a large excess of diethyl ether slowly precipitated crystals of crown ether complexed potassium dicarbonylbis(triphenylphosphite)rhodate(−1). The structure of this complex has been determined by single crystal X-ray diffrac-

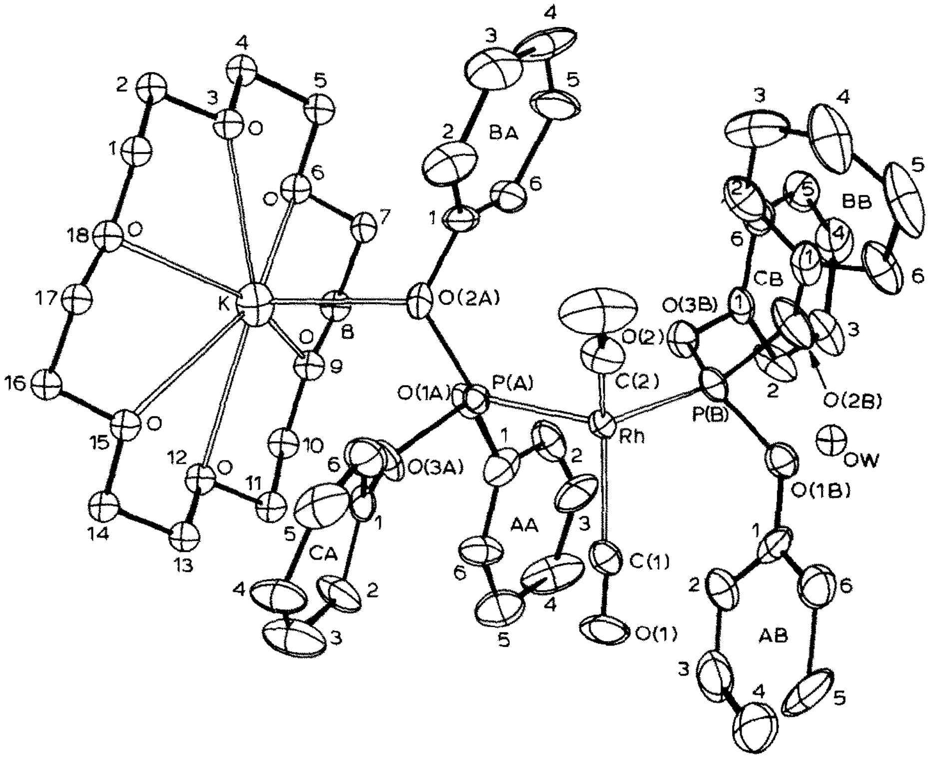

Fig. 3. A perspective view of $[K(C_{12}H_{24}O_6)][Rh(CO)_2(P(OPh)_3)_2]$. Principle bond lengths (Å): Rh–P(A), 2.159; Rh–P(B), 2.212; Rh–C(1), 1.972; C(1)–O(1), 1.079; C(2)–O(2), 1.103; K–O(2A), 2.829. Principle bond angles (degrees): P(A)–Rh–P(B), 108.8; P(A)–Rh–C(1), 107.7; P(A)–Rh–C(2), 108.2; P(B)–Rh–C(1), 110.9; P(B)–Rh–C(2), 112.5; C(1)–Rh–C(2), 108.6; Rh–C(1)–O(1), 176; Rh–C(2)–O(2), 178.

tion. A perspective view of this complex is shown in Fig. 3. It is of interest to note that in this complex the crown ether bound potassium cation ion-pairs to the anion through one of the oxygen atoms in a triphenylphosphite ligand. The most obvious difference between the 18-crown-6 ether complexed potassium cation and its sodium analog is that the potassium ion fits perfectly in the crown ether with minimal distortion of the crown ether ring.

Protonation of rhodium anions

Anionic rhodium complexes such as $[Rh(CO)_3L]^-$ and $[Rh(CO)_2L_2]^-$ are fairly strong bases. Even relatively weak acids such as water and alcohols protonate them to form the corresponding hydride species. Because some of these rhodium hydrides are unstable, decomposition products are often observed. Thus, when methanol is added to a THF solution of a mixture of $[Rh(CO)_4]^-$, $[Rh(CO)_3(PPh_3)]^-$ and PPh_3 (from the sodium amalgam reduction of $RhCl(CO)(PPh_3)_2$ under CO), a yellow dimer, $(PPh_3)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)_2(PPh_3)$, is obtained. ($\nu$(CO) 2018s, 1988vs, 1799s, 1774vs cm^{-1}.) The structure of this dimer has been determined by X-ray diffraction and the results have been reported in a communication [7]. A possible mechanism for the formation of this complex is outlined below.

$$\begin{tikzcd}
\begin{array}{c}[Rh(CO)_x(PPh_3)_{4-x}]^- \\ (x = 3 \text{ or } 4)\end{array} \arrow[r, shift left, "CH_3OH"] & HRh(CO)_x(PPh_3)_{4-x} \arrow[l, shift left] \arrow[d, "PPh_3"', "\begin{array}{l}-H_2, \\ \text{Dimerization} \\ \text{and ligand} \\ \text{substitution}\end{array}"] \\
 & (PPh_3)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)_2(PPh_3)
\end{tikzcd}$$

The preferential formation of the pentacarbonyltris(triphenylphosphine)dirhodium species instead of the previously suggested tetracarbonyltetrakis(triphenylphosphine)dirhodium complex [9] was initially thought to be caused by the steric hindrance of the bulky triphenylphosphine ligands. However, upon further study of this reaction with a variety of phosphine ligands, we have found that the preferred $Rh_2(CO)_5L_3$ structure is not limited to bulky phosphine ligands. When excess of PPh_2Me, $PPhMe_2$, and PMe_3 were used as ligands in this reaction, $Rh_2(CO)_5(PPh_2Me)_3$ (ν(CO) (THF) 1983, 1963, 1752, 1734 cm^{-1}), $Rh_2(CO)_5(PPhMe_2)_3$ (ν(CO) (THF) 1969, 1951, 1746, 1726 cm^{-1}), and $Rh_2(CO)_5(PMe_3)_3$ (ν(CO) (THF) 1960, 1941, 1743, 1724 cm^{-1}), respectively, were formed. Since trimethylphosphine is relative small, it appears to us that the formation of the trisphosphine dimer is due to some sort of balance of electronic effects instead of pure steric effect. Recently James et al. [10] reported the synthesis of a class of rhodium dimers of the form $[L_2(CO)Rh(\mu(CO)]_2$ (L_2 is a bidentate chelating phosphine ligand). In those cases only two infrared stretching frequencies are observed for each dimer owing to the presence of higher symmetry.

Experimental

General data

All operations were carried out either under N_2 in an inert atmosphere glove box or under CO in a Fisher-Porter bottle. All reagents were purified according to standard, published methods and degassed before use. Infrared spectra were recorded on a Nicolet MX-1 spectrometer. The high pressure infrared spectroscopic studies were carried out in a high pressure infrared cell [11]. X-ray crystallographic data were collected on a Syntex $P2_1$ automated diffractometer.

(A) Isolation of single crystals of $[Na(C_{12}H_{24}O_6)][Rh(CO)_3(PPh_3)]$

One gram of $RhCl(CO)(PPh_3)_2$ was stirred in 50 ml THF over 100 g 1% sodium amalgam under 60 psi CO in a Fisher–Porter bottle at 60 °C for 20 h. The CO was vented and the solution was filtered under vacuum and then transferred to a 4 ounce glass bottle with a screw cap. 0.5 g 18-crown-6 ether was dissolved in the solution and three small test tubes which were filled with diethyl ether were placed inside the glass bottle. (The level of the light yellow solution of the Rh complexes was at about half the height of the test tubes.) The bottle was capped tightly and placed in a dry box for two days to allow the diethyl ether to diffuse into the THF solution. Yellow crystals were found to deposit on the walls of the bottle and the test tubes. The solution was decanted and the crystals were careful rinsed with diethyl ether. They were mounted and sealed in capillary tubes in degassed paraffin oil. (The paraffin oil protected the crystals from air while they were being mounted.)

(B) Isolation of single crystals of $[Na(THF)_2][Rh(CO)_2(Diphos)]$

One gram of RhCl(CO)(Diphos) was stirred in 50 ml THF over 100 g 1% sodium amalgam under 60 psi CO in a Fisher–Porter bottle at ambient temperature for 20 h. The solution was filtered under vacuum and then stirred under nitrogen atmosphere for one week. Crystals were grown using the same method as in (A) except that no crown ether was used.

(C) Isolation of single crystals of $[K(C_{12}H_{24}O_6)][Rh(CO)_2(P(OPh)_3)_2]$

0.28 gram $[Rh(CO)_2Cl]_2$ and 1.0 g $P(OPh)_3$ were stirred in 50 ml of THF over 100 g 1% potassium amalgam under 60 psi CO in a Fisher bottle at ambient temperature for 20 h. The colorless solution was filtered under vacuum and then stirred under a nitrogen atmosphere for one week. 0.5 g 18-crown-6 ether was dissolved in the solution and crystals were grown using the same method as in (A).

X-Ray Crystallographic Analysis of $[Na(C_{12}H_{24}O_6)][Rh(CO)_3(PPh_3)]$

The crystallographic data are summarized in Table 1. The reflection data were collected employing Cu-$K_{\bar{\alpha}}$ radiation (λ 1.5418 Å) at about −140 °C. The structure was solved by Patterson heavy atom methods and refined by a block diagonal least squares procedure to a discrepancy factor of 0.125 based on 2835 observed reflections. The crown ether molecule shows a great degree of disorder even at low temperature. The atoms C(11E), C(12E), C(14E), and C(15E), which are at the turning points of the crown ether conformation tend to drift along a-axis. Their positional and thermal parameters were hence fixed in the final few cycles of refinements.

X-Ray crystallographic analysis of $[Na(THF)_2][Rh(CO)_2(Diphos)]$

The crystallographic data are summarized in Table 1. X-ray diffraction data were collected under Cu-K_α (λ 1.5418 Å) radiation. Three standard reflections (012, $\bar{2}0\bar{3}$, 313) were measured after every 97 reflections had been collected. These monitor reflections showed 30–35% intensity drop during the period of data collection. The raw data were corrected by anisotropic decay and Lorentz-polarization factors.

TABLE 1

CRYSTALLOGRAPHIC DATA

Complex	$[Na(C_{12}H_{24}O_6)][Rh(CO)_3(PPh_3)]$	$[Na(THF)_2][Rh(CO)_2(Diphos)]$	$[K(C_{12}H_{24}O_6)][Rh(CO)_2(P(OPh)_3)_2]$
Formula	$C_{33}H_{39}O_9NaPRh$	$RhP_2NaO_4C_{36}H_{40}$	$RhKP_2O_{14}C_{50}H_{54}$
M.W.	736.5	724.6	1082.9
a, Å	10.847(5)	11.737(4)	11.178(4)
b, Å	13.156(5)	20.232(7)	26.979(4)
c, Å	13.200(6)	14.718(9)	18.114(5)
α, degree	73.53(3)	90	90
β, degree	72.48(3)	93.66(4)	92.68(2)
γ, degree	88.74(3)	90	90
V, Å^3	1718(1)	3488(3)	5420(2)
Z	2	4	4
d calc, g cm^{-3}	1.42	1.38	1.33
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
$F(000)$	760	1552	2240
Crystal shape	parallelepiped prism	green yellowish rod	colorless parallelepiped prism
Crystal size	$0.5 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.5$	$0.5 \times 0.4 \times 0.5$
μ, cm^{-1}	51.2 (Cu-K_α)	53.8 (Cu-K_α)	5.0 (Mo-K_α)
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$
Scan type	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$
Scan rate, deg min^{-1}	2.–19.5	2.–19.5	2.–19.5
Scan range, deg	2	2	2
2θ (max), deg	120	120	50
Number of unique reflections	4734	4692	9600
Number of reflections with $I > 2.33\ \sigma(I)$	2835	3418	5134
No. of variables	407	494	455
R (obsd reflections)	0.120	0.0608	0.1148
R_w (obsd reflections)	0.142	0.0764	0.1535
Goodness of fit	2.861	2.049	3.95

Absorption correction was done empirically by using ψ scan data. The structure was solved by Patterson heavy atom method and refined by a full matrix least squares procedure. Most of the computer programs employed are from the SDP crystallographic package [12].

X-Ray crystallographic analysis of $[K(C_{12}H_{24}O_6)][Rh(CO)_2(P(OPh)_3)_2]$

The crystallographic data are summarized in Table 1. X-ray diffraction data were collected under Mo-$K_{\bar{\alpha}}$ (λ 0.7107 Å) radiation. Three standard reflections ($2\bar{2}\bar{2}$, $\bar{1}\bar{6}7$, $3\ 16\ \bar{1}$) were used to monitor the data collection. Their intensities did not show significant deviations within the period of data collection. The raw data were corrected by Lorentz-polarization factor. The structure was solved by Patterson heavy atom method. During the refinement process it was found that the crown ether molecule in the crystal was highly disordered. Roughly two major sites were found from the difference Fourier map. Two half-occupied molecules with idealized geometry were put in these two sites with all atoms having isotropic temperature factor 20.0. The positional and thermal parameters at the crown ether molecules were kept fixed during the refinement. The discrepancy factor was 0.177 if the crown ether was omitted from the structure and 0.117 if it was included. The residual electron density was mostly around the crown ether area, indicating that the crown ether molecule actually occupies more than the current two major sites.

Apart from the residual electron density in the vicinity of the disordered crown ether, there was one large peak of residual electron density in the difference Fourier synthesis. This peak was located near an inversion center in an empty hole in the lattice 4.4 Å from the nearest atom. The amplitude of the peak, 1.5 e/Å^3, corresponded to 35–50% of an oxygen atom. The peak is 1.31 Å away from its symmetry related partner. Infrared spectra of single crystals of this material showed no evidence for water or free CO in the lattice. This residual was arbitrarily refined as an oxygen atom at 50% occupancy (OW). Including this peak in the least squares refinement improved the discrepancy indices from $R(F) = 0.117$ and $R_w(F) = 0.163$ to $R(F) = 0.115$ and $R_w(F) = 0.153$.

Acknowledgment

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