

Figure 1. EPR spectra at 25 K of Fe(TPP)Cl in toluene-methanol (5:2 v/v) in the absence or presence of the MeO⁻ anion: [Fe(TPP)Cl]₀ = 1.4 × 10⁻³ M, [MeO⁻]₀/[Fe(TPP)Cl]₀ = 0 (a), 2 (b), 10 (c), and ~50 (d). The spectra indicate three complex species in the solutions. They are assigned to Fe(TPP)Cl (high spin; $g_x = g_y = 6.03$, $g_z = 2.00$), Fe(TPP)(OMe) (high spin; $g_x = 5.55$, $g_y = 6.40$, $g_z = 1.99$), and Fe(TPP)(OMe)₂⁻ (low spin; $g_x = 1.914$, $g_y = 2.165$, $g_z = 2.494$) with the spin state and g values in parentheses.

in Table I. The tetragonal and rhombic splittings in the three t_2 orbitals, δ and μ , respectively, the crystal field rhombicity R , and the orbital reduction factor k fall within the parameter ranges allowable for the analysis based on the pure t_2^5 configuration, indicating that Fe(TPP)(OMe)₂⁻ is unambiguously in the low-spin ground state.

In Table I are listed, for comparative purpose, the crystal field parameters for the corresponding complexes with axial ligation mode S-Fe-S, Fe(PPIXDME)(S-*n*-Bu)₂⁻ and Fe-(PPIXDME)(SC₆H₄-4-NO₂)₂⁻.¹⁶ It is generally accepted that the anionic O-donor ligands RO⁻ and PhO⁻ are weaker in ligand field strength than the corresponding thiolates RS⁻ and PhS⁻, which manifests itself in the difference in spin states between Fe(PPIXDBE)(OC₆H₄-4-NO₂)₂⁻ and Fe-(PPIXDME)(SC₆H₄-4-NO₂)₂⁻. In view of this, the greater δ value for Fe(TPP)(OMe)₂⁻ compared with Fe-(PPIXDME)(S-*n*-Bu)₂⁻ is at first sight somewhat surprising. However, such apparent discrepancy may be removed, if we remember that the spin state is determined mainly by metal-ligand σ bonding, while δ and μ are affected by π bonding.¹⁷ It seems that the axial ligation mode O-Fe-O gives the largest δ value among the six types of axial ligation modes.^{1,10} The smaller μ and R values are consistent with the trend in crystal field rhombicity (E/D) found in five-coordinate high-spin Fe(III) porphyrin complexes with RO⁻, PhO⁻, and PhS⁻ as axial ligands.^{1,13,18}

Registry No. Fe(TPP)(OMe)₂⁻, 89709-81-9; Fe(TPP)Cl, 16456-81-8; Fe(TPP)(OMe), 29189-59-1.

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 (17) Qualitatively, δ increases with the increasing π -donor strength of the axial ligand, while it decreases with increasing π -acceptor strength. The smaller δ value in S-Fe-S may be the result of partial cancellation of the two effects. In contrast, there is evidently no such cancellation in O-Fe-O, resulting in a larger δ .
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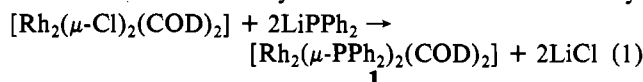
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Further Examples of Binuclear Phosphido-Bridged Complexes of Rhodium(I). Evidence for Bridge-Cleavage Reactions

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Meek and co-workers¹⁻⁴ have reported the preparation and properties of several diphenylphosphido-bridged polynuclear complexes of Rh. During the course of our studies of *heteronuclear* phosphido-bridged complexes of Rh,⁵⁻⁸ we also had the occasion to prepare and examine several new *homonuclear* phosphido-bridged Rh complexes that complement those described by Meek and Kreter.^{3,4} These workers prepared [Rh₂(μ -PPh₂)₂(COD)₂] (1) (COD = 1,5-cyclooctadiene) by reaction 1 and extensively studied its derivative chemistry.



They showed that both COD ligands of 1 can be replaced by chelating diphosphine ligands but that only one COD can be substituted by tertiary phosphines under normal thermal conditions.

We show herein that LiPMePh works equally well in these syntheses, that *mono*(phosphido)-bridged complexes can be easily prepared by control of the reaction stoichiometry of eq 1, and that monodentate phosphines can indeed replace both COD ligands when the substitution reactions are carried out under an H₂ atmosphere. We also describe results which demonstrate that reversible dissociation of these binuclear complexes into mononuclear fragments must occur during the course of some of their reactions.

Experimental Section

[Rh₂(μ -Cl)₂(COD)₂],⁹ LiPPh₂,¹⁰ LiPMePh,¹⁰ and [Rh₂(μ -PPh₂)₂(COD)₂]³ were prepared according to literature procedures. PPh₂H, PMePhH, PEt₃ (Strem Chemical Co.), and 1,5-cyclooctadiene (Aldrich Chemical Co.) were obtained commercially. Solvents and liquid chemicals were dried by standard methods, and all reactions were carried out under a prepurified N₂ atmosphere by using standard Schlenk techniques.¹¹ All reported ³¹P NMR chemical shifts are relative to external H₃PO₄ with downfield shifts positive. The ³¹P NMR spectrum of [Rh₂(μ -PPh₂)₂(PEt₃)₄] was simulated so external to extract accurate coupling constants by using the program "Parameter Adjustment in NMR by Iteration Calculation" (PANIC), an Aspect 2000 NMR software package. Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

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Preparation of $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$. Method A. To a solution containing 0.150 g (0.30 mmol) of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ in 40 mL of THF was added 20 mL of a THF solution containing 0.169 g (0.77 mmol) of LiPMePh. The $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ solution rapidly changed color from yellow to dark greenish brown as the yellow-orange solution of LiPMePh was added dropwise. The solution was allowed to stir at 22 °C for 1 h. The solvent was removed under vacuum, and the reaction mixture was extracted by addition of 70 mL of benzene and then filtered through Celite 545. The solvent was removed from the filtrate under vacuum, and the residue was triturated with hexane to remove any entrapped benzene. Evaporation of the hexane gave dark greenish brown microcrystalline $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$ (0.164 g, 0.25 mmol) in 82% yield. Anal. Calcd for $\text{C}_{30}\text{H}_{46}\text{P}_2\text{Rh}_2$: C, 53.92; H, 5.98. Found: C, 52.22; H, 6.40. $^{31}\text{P}\{^1\text{H}\}$ NMR, C_6D_6 solution: δ -43.69 t ($^3J_{\text{P-Rh}} = 98.8$ Hz), δ -93.20 t ($^3J_{\text{P-Rh}} = 100.6$ Hz). The integrated intensity ratio of the δ -43.69 triplet relative to that of the δ -93.20 triplet was 2.9:1.

Method B. The above synthesis was also carried out at -90 °C by using a 2-propanol slush bath. After the reactants were stirred for 3 h at -90 °C, the temperature was raised to -45 °C, and the solvent was removed under vacuum. The rhodium complex was extracted from the LiCl byproduct and unreacted LiPMePh with toluene at -35 °C, followed by filtration. The toluene was removed from the filtrate under vacuum at a temperature that did not exceed -10 °C. The ^{31}P NMR spectrum of this material recorded in C_6D_6 solution at 22 °C showed the same resonances as above but in an integrated intensity ratio of 0.95:1. After the sample was allowed to stand at 22 °C for 48 h, the intensity ratio of these resonances changed to ~3.1:1.

Preparation of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$. To a solution containing 1.464 g (2.97 mol) of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ in 150 mL of THF was added 60 mL of a THF solution containing 0.663 g (2.7 mmol) of LiPPh₂. The $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ solution gradually changed from yellow to light green as the yellow-orange solution of LiPPh₂ was added dropwise over a period of 2 h. The solution was allowed to stir at room temperature for 1 h. The solvent was removed under vacuum, and the rhodium complex was extracted from the LiCl byproduct by addition of 60 mL of benzene, followed by stirring and filtration through Celite 545. The solvent was removed from the filtrate under vacuum, and $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$ was separated from unreacted $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ by extraction with diethyl ether. Removal of the diethyl ether under vacuum gave green microcrystalline $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$ (1.240 g, 1.93 mmol) in 65% yield based on $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$. Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{ClPRh}_2$: C, 52.33; H, 5.29. Found: C, 52.15; H, 5.11. m/z (fast atom bombardment): 642 (M^+), 607 ($\text{M}^+ - \text{Cl}$), 565 ($\text{M}^+ - \text{Ph}$), 536 ($\text{M}^+ - \text{COD}$).

Preparation of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PMePh})(\text{COD})_2]$. To a solution containing 0.220 g (0.45 mmol) of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ in 50 mL of THF was added 40 mL of a THF solution containing 0.076 g (0.35 mmol) of LiPMePh. The $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ solution gradually changed from yellow to greenish brown as the yellow solution of LiPMePh was added in a dropwise manner over a period of 1 h. The solution was allowed to stir at room temperature for 1 h, and the product was worked up in the same manner as described above for $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$, resulting in the isolation of greenish brown microcrystalline $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PMePh})(\text{COD})_2]$ (0.135 g, 0.23 mmol) in 52% yield based on $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$. Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{ClPRh}_2$: C, 47.58; H, 5.51. Found: C, 46.86; H, 6.50.

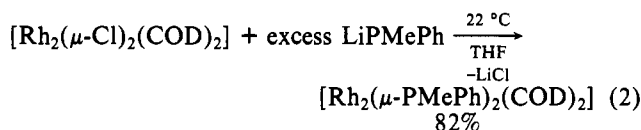
Preparation of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PET}_3)_4]$. To a solution containing 0.212 g (0.27 mmol) of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ in 40 mL of benzene was added 0.159 mL (1.07 mmol) of PET_3 via a syringe. The solution immediately changed in color from dark green to reddish brown. H_2 was then introduced into the flask, and the solution was allowed to stir for 30 min, during which time the solution became dark red. The solution was concentrated to a volume of approximately 2 mL and was passed through a 38 × 2 cm chromatography column packed with Bio-Beads SX-12 using benzene as eluant. Bio-Beads procedure separated the product from excess PET_3 . A red band was collected, and the benzene was removed under vacuum. The resulting red residue was redissolved in 25 mL of hexane to remove entrapped benzene. The hexane was then removed under vacuum, resulting in the isolation of red microcrystalline $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PET}_3)_4]$ (0.230 g, 0.22 mmol) in 81.3% yield. Anal. Calcd for $\text{C}_{48}\text{H}_{80}\text{P}_6\text{Rh}_2$: C, 54.99; H, 7.63. Found: C, 53.74; H, 7.21.

Reaction of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$. A sample of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ for ^{31}P NMR monitoring was

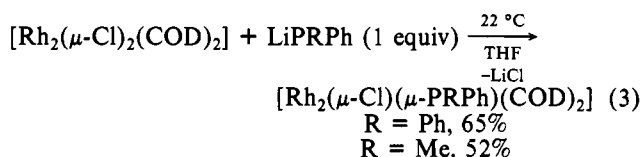
prepared by dissolving 0.030 g (0.04 mmol) in 3 mL of C_6D_6 . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded, and then 1 equiv of solid $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ (0.018 g, 0.04 mmol) was added. The sample was heated at 60 °C for 9 h, after which the $^{31}\text{P}\{^1\text{H}\}$ spectrum was again recorded. The spectrum showed two triplets, one at δ -71.5 due to $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ and one at δ 21.6 due to $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$ in an integrated intensity ratio of ~3:1. The sample was heated for another 5 h, after which the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed only the resonance of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$.

Results

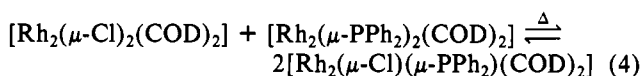
Syntheses. The method used for the synthesis of the binuclear phosphido-bridged complexes reported herein is the same as that employed by Meek and Kreter^{3,4} for the preparation of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$, eq 1, namely the reaction of LiPR₂ derivatives with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$. We find that Meek's method can be extended to the use of LiPMePh to give $\mu\text{-PMePh}$ derivatives, eq 2, and probably to other LiPR₂ de-



rivatives as well. Significantly, we find that the use of 1 equiv of the LiPR₂ reagent allows the preparation of mono(phosphido)-bridged complexes of the type $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PR}_2)(\text{COD})_2]$ in reasonable yields, eq 3. The mono(phosphi-

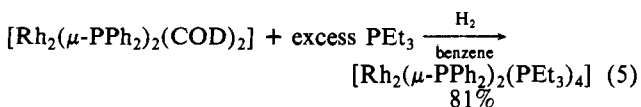


do)-bridged derivatives can also be prepared simply by heating a mixture of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ and $[\text{Rh}_2(\mu\text{-PR}_2)_2(\text{COD})_2]$, eq 4 (see Experimental Section). While this reaction is likely



an equilibrium process, the equilibrium must lie far to the right since prolonged heating (~14 h) drives the reaction completely to the mono(phosphido)-bridged product, as evidenced by the ^{31}P NMR spectrum of the final solution, which shows only the resonance of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$.

Meek and Kreter^{3,4} have reported that only one COD ligand in $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ can be substituted by monodentate phosphines under normal thermal conditions. On the other hand, $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ is a potent hydrogenation catalyst,³ as the COD ligands can apparently be removed by hydrogenation. We thus conducted the substitution reaction with PET_3 under an H_2 atmosphere. Under such conditions, replacement of both COD ligands occurs to give $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PET}_3)_4]$ in excellent yield, eq 5. Although only the



reaction with PET_3 was examined in detail, preliminary data indicate analogous reactions with PMe_3 , PPh_2Bu , and PPh_2Me .

Characterization of the New Complexes. All of the binuclear compounds described herein were characterized by C, H analyses and by their ^{31}P NMR spectra. In addition, a fast-atom-bombardment mass spectrum of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$ showed parent and fragment ions consistent with the molecular stoichiometry. These compounds are all unstable with respect to Al_2O_3 and SiO_2 chromatography and are difficult to obtain in rigorously pure form. ^{31}P NMR spectra of carefully recrystallized samples of $[\text{Rh}_2(\mu\text{-$

Table I. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectral Data in C_6D_6 Solution

complex	$\delta(\mu\text{-PR}_2)$	$J^{31}\text{P}-^{103}\text{Rh}$, Hz
$[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$	-70.58 t	100.3
$[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$	-43.69 t	98.8
	-93.20 t	100.6
$[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{COD})_2]$	23.19 t	112.3
$[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PMePh})(\text{COD})_2]$	8.90 t	111.2
$[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_4]^a$	184.9 t	166.0
	of quint	

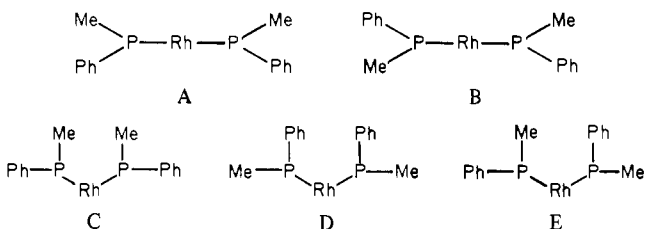
^a $J^{31}\text{P}_{\mu-^{31}\text{PEt}_3} = 18.9$ Hz; $\delta = -14.2$ m (4 PEt_3 , $^1J^{31}\text{P}_{\text{Et}^-^{103}\text{Rh}} = 128.7$ Hz, $^3J^{31}\text{P}_{\text{Et}^-^{103}\text{Rh}} = 26.0$ Hz).

$\text{PMePh})_2(\text{COD})_2]$, for example, always showed a small amount of $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-PMePh})(\text{COD})_2]$ to be present, an observation that accounts for the persistently low C, H analysis for this material.

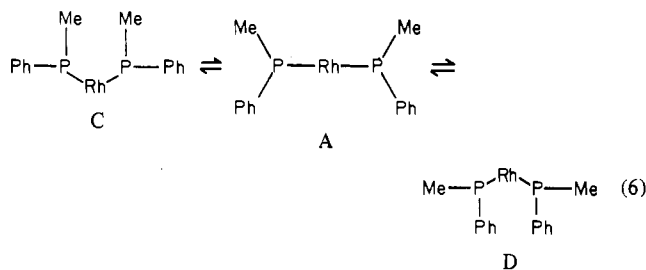
^{31}P NMR data for the complexes discussed herein are summarized in Table I. In each case the bridging $\mu\text{-PR}_2$ ligands appear as a triplet exhibiting coupling to two equivalent Rh nuclei. In accord with other studies,¹² the upfield positions of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances imply that these ligands bridge two Rh centers that are not connected by a direct metal-metal bond.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$ shows two triplets at $\delta -43.69$ and -93.20 whose relative integrated intensity depends upon the conditions employed in the synthesis of the compound. As noted in the Experimental Section, when the synthesis of $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$ was carried out at 22°C , the integrated intensity ratio of the $\delta -43.69$ to $\delta -93.20$ resonances was approximately 3:1. When this compound was prepared at -90°C , an approximate 1:1 ratio was observed. Significantly, when a solution containing a sample from the low-temperature preparation was allowed to stand at room temperature for 48 h, the intensity ratio slowly changed to $\sim 3:1$. This change does not reverse upon returning the sample to -90°C .

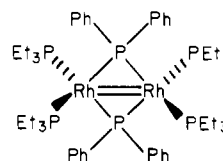
We attribute these two resonances of $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$ to two isomeric forms of the molecule that have different dispositions of the substituents of the phosphido bridges. A priori, structures with bent and planar $\text{Rh}_2(\mu\text{-P})_2$ cores must be considered, and drawings A-E illustrate the



possible isomers. The COD ligands have been omitted for clarity, and the view is down the Rh-Rh axis. The ^{31}P NMR spectra could reflect the presence of the two planar isomers (A, B) or two of the three bent isomers (C, D, E). However, isomers C and D could rapidly interconvert by a simple "flapping" of the molecules as in eq 6, a process which easily occurs for bis(phosphido)-bridged complexes of Fe and Co.^{13,14} Thus these spectra could represent a mixture of isomer E and the C/D exchange-averaged isomer of the bent structure.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_4]$ (Figure 1, supplemental) consists of a triplet of quintets centered at $\delta 184.9$ attributed to the $\mu\text{-PPh}_2$ ligands and a complex multiplet at $\delta -14.2$ assigned to the PEt_3 ligands. The overall pattern is similar to that of $[\text{Rh}_2(\mu\text{-PHBu-}t)_2(\text{PMe}_3)_4]$, which was recently characterized by Jones et al.¹⁵ The downfield chemical shift of the bridging diphenylphosphido ligands strongly argues for the presence of a metal-metal bond,¹² and the relatively small value for the $^{31}\text{P}_{\text{Et}^-^{31}\text{P}_{\mu}}$ coupling constant (18.9 Hz) implies a distorted tetrahedral geometry about each Rh center:



A Rh-Rh double bond is required to give each metal a satisfactory electron count. The structure suggested for $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_4]$ is analogous to those crystallographically demonstrated for $[\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2]$,¹⁶ $[\text{Ir}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\text{PPh}_3)_2]$,¹⁷ and $[\text{Rh}_2(\mu\text{-PHBu-}t)_2(\text{PMe}_3)_4]$,¹⁵ with which it is isoelectronic.

The $[\text{Rh}_2(\mu\text{-PR}_2)_2(\text{COD})_2]$ complexes were found to be stable in air in the solid state for several hours although the $[\text{Rh}_2(\mu\text{-PR}_2)(\mu\text{-Cl})(\text{COD})_2]$ complexes and $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{PEt}_3)_4]$ decompose within minutes when solid samples are air-exposed. All of the complexes are extremely air sensitive in solution. All are very soluble in THF, CH_2Cl_2 , and aromatic hydrocarbons and slightly to moderately soluble in Et_2O and aliphatic hydrocarbons.

Discussion

In addition to extending the synthetic methodology previously described by Meek and Kreter,³ this study has also provided important evidence for the fact that the $\mu\text{-PR}_2$ ligands in these complexes are not sufficient to retard disruption of some of the dimeric units in solution. There are two pieces of evidence that lead to this conclusion. First is the quantitative synthesis of $[\text{Rh}_2(\mu\text{-PPh}_2)(\mu\text{-Cl})(\text{COD})_2]$ from the 60°C reaction of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$, eq 4. Although the details of the mechanism of this reaction are unknown, it is clear that disruption of the $\text{Rh}_2(\mu\text{-PPh}_2)_2$ core of $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{COD})_2]$ must occur.

Fragmentation of the dimers must also occur during the interconversion of the isomers of $[\text{Rh}_2(\mu\text{-PMePh})_2(\text{COD})_2]$ described above. Recall that at -90°C the isomers are present in a 1:1 ratio, but upon warm-up and standing at 22°C for 48 h, the isomer ratio changes to $\sim 3:1$. It is impossible for the two isomers to interconvert by an intramolecular process, and Rh-($\mu\text{-PMePh}$) bonds must break during this rearrangement. The simplest mechanism that would account for

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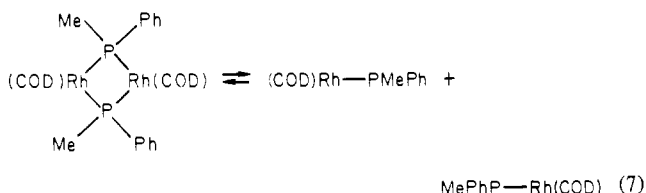
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the isomerization is reversible dissociation into monomeric complexes as in eq 7. A more complicated mechanism in-



volving initial dissociation of only one Rh-P bond followed by association of the resultant free Rh-PMePh ligand with a Rh center of another dimeric complex can also be envisaged. Although the isomerization is relatively slow at 22 °C, requiring ~1 day for equilibrium to be reached, the essential point is that isomerization does occur and the μ -PMePh bridging ligands are clearly not sufficient to retard fragmentation of the binuclear complexes. A similar conclusion was reached in our earlier study of a series of μ -PPh₂-bridged cobalt carbonyl complexes.¹⁸

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Registry No. 1, 82829-24-1; [Rh₂(μ -PMePh)₂(COD)₂], 89908-32-7; [Rh₂(μ -Cl)(μ -PPh₂)(COD)₂], 83681-89-4; [Rh₂(μ -Cl)(μ -PMePh)(COD)₂], 89908-33-8; [Rh₂(μ -PPh₂)(PEt₃)₄], 89908-34-9; [Rh₂(μ -Cl)₂(COD)₂], 12092-47-6; LiPMePh, 38327-00-3; LiPPh₂, 4541-02-0.

Supplementary Material Available: Figure 1, ³¹P{¹H} NMR spectrum of [Rh₂(μ -PPh₂)(PEt₃)₄] in C₆D₆ solution (1 page). Ordering information is given on any current masthead page.

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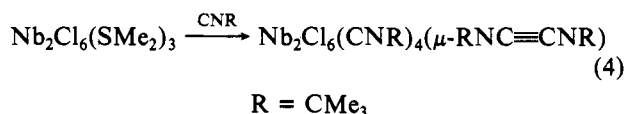
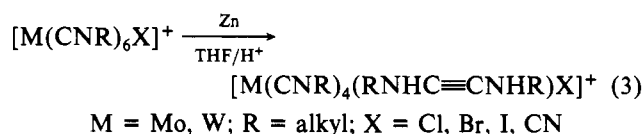
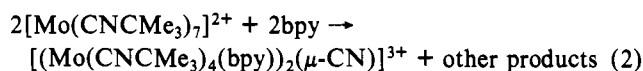
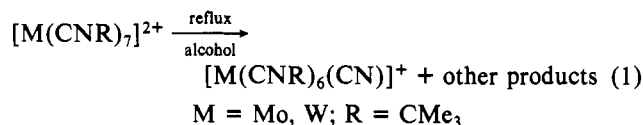
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Synthesis and Structure of [(η^5 -C₅H₅)Nb(CNCMe₃)₄Cl][NbOCl₄(THF)]·THF^{1,2}

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High-coordinate early transition metal isocyanide complexes have been of interest to us for several reasons. Because the C≡N-R unit is sterically undemanding, M(CNR)_xL_{n-x} (L = halide, cyanide, etc.; n > 6) complexes afford an opportunity to explore relationships among electronic structure, crystal packing forces, and stereoisomerism for this class of compounds.^{2,3} The chemistry of these isocyanide complexes has also proved to be quite intriguing, especially the recently discovered dealkylation (eq 1, 2)^{4,5} and reductive coupling^{6,7} (eq 3, 4) reactions. Although a variety of isocyanide complexes



of the group 6 metals now exists, there has been much less work on group 5 isocyanide complexes.⁸ Known examples include six-coordinate vanadium compounds,⁹ some incompletely characterized niobium and tantalum "insertion products" of RNC into M-halogen bonds,¹⁰ the crystallographically identified compounds Nb₃Cl₈(CNCMe₃)₅ and Nb₂Cl₆(CNCMe₃)₄(μ -Me₃CNCCNCMe₃),⁷ and the bis(cyclopentadienyl) complexes [(η^5 -C₅H₅)₂NbCl(CNR)], R = Ph, Cy.¹¹ In the present note we describe the synthesis and structural characterization of [(η^5 -C₅H₅)Nb(CNCMe₃)₄Cl]⁺, a formally eight-coordinate niobium(III) (d²) cation analogous in some respects to the niobium(III) center in Nb₂Cl₆(CNCMe₃)₄(μ -Me₃CNCCNCMe₃).

Experimental Section

Synthesis of [(η^5 -C₅H₅)Nb(CNCMe₃)₄Cl][NbOCl₄(THF)]·THF. Preparative work was carried out under an atmosphere of nitrogen with use of dried, distilled solvents. The starting material (η^5 -C₅H₅)NbCl₄ was prepared from (η^5 -C₅H₅)Sn(*n*-C₄H₉)₃¹² by a literature procedure.¹³ Sodium amalgam (1%, 2 mL) was added to a mixture of (η^5 -C₅H₅)NbCl₄ (1 g, 3.33 mmol) and CNCMe₃ (1.8 mL, 16.7 mmol) in 40 mL of toluene and 10 mL of THF. The mixture was stirred at room temperature for 20 min. After this time all the sparingly soluble starting material had reacted to give a brown-orange solution, which was filtered through Celite. The filtrate was evaporated in vacuo to give a partly crystallized brown oil. The product was obtained as bright orange needles by two recrystallizations from THF (15 mL) and heptane (~10 mL) at -20 °C. The air-sensitive crystals were washed with heptane and dried in vacuo; yield 0.5 g (32%). Anal. Calcd for Nb₂Cl₅O₃N₄C₃₃H₅₇: C, 43.04; H, 6.24; N, 6.08; Cl, 19.25. Found: C, 43.58; H, 6.29; N, 6.37; Cl, 18.99. IR (Nujol): ν_{CN} , 2185 (s, sh), 2146 (vs), 2048 (m, sh) cm⁻¹; other, 1283 (m), 1198 (s), 1065 (m), 1038 (m), 1010 (m), 962 (s, ν_{NbO}) cm⁻¹. NMR (CDCl₃): δ 5.02 s (5 H), η^5 -C₅H₅; 3.96 m (8 H), O-CH₂ (THF); 1.88 m (8 H)

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