The crystalline packing of $C_6F_4Fe_2(CO)_8$, as shown in Figure 4, has no intermolecular contacts significantly below those predicted from sums of van der Waals radii.

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Registry No. $(CH_3)_3SiCl$, 75-77-4; $Li[(CO)_4FeC(O)C_6H_5]$, 41765-66-6; $C_6F_4Fe_2(CO)_8$, 29160-38-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2944.

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Binuclear Nitrosyl Complexes. Synthesis and Structure Determination of Dinitrosylbis(μ-diphenylphosphido)-bis(tertiary phosphine)diruthenium, $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ ($L = PMePh_2, PPh_3$)

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The binuclear complexes $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ ($L = PMePh_2, PPh_3$) have been synthesized and the structure of the methyldiphenylphosphine complex has been determined by single-crystal X-ray methods using intensity data collected by the θ-2θ scan technique. $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 13.12$ (1), $b = 12.95$ (1), $c = 15.94$ (2) Å, $\beta = 120.2$ (1)°, and $V = 2341$ Å^3. The experimental and calculated densities of 1.46 (2) and 1.47 g/cm^3 agree for two dimer units per unit cell. The structure was solved by standard Patterson and Fourier methods and has been refined by a least-squares procedure to a final R factor of 0.054 for 1659 reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimeric complex is crystallographically required to be centrosymmetric with the ruthenium atoms bridged by diphenylphosphido groups. The coordination geometry about each Ru atom (excluding the Ru-Ru bond) is a distorted tetrahedron. The nitrosyl is terminally coordinated in a linear manner with an Ru-N distance of 1.697 (12) Å and an Ru-N-O bond angle of 174.1 (10)°. The Ru-Ru distance of 2.629 (2) Å is relatively short compared with corresponding values in ruthenium cluster compounds and is consistent with the formulation of the Ru-Ru bond in these systems as a metal-metal double bond. The Ru-P distances in the structure are 2.315 (4) Å for the terminal phosphine ligand and 2.304 (4) Å for the bridging phosphide ligands. The syntheses of the binuclear complexes were devised after the structure determination of the methyldiphenylphosphine system was completed. It involves the *in situ* generation of $LiPPh_2$ as the way for introducing the bridging ligands.

Introduction

Nitric oxide has been postulated to activate metal ions in catalytically active complexes by virtue of its dual coordinating ability.[1] This ability, which has been described as amphoteric behavior,[1,2] manifests itself structurally in the linear and bent modes of nitrosyl coordination corresponding, at least formally, to NO^+ and NO^-, respectively.[2-6] Interconversion between these two bonding modes was proposed in 1969 by Collman, *et al.*,[1] who viewed the nitrosyl ligand acting as an electron pair sink and pump in catalytically active complexes. This interconversion of bonding modes was considered in terms of an intramolecular redox reaction[1,7] during which a stereochemical change occurs at the metal center concomitantly with the bending and straightening of the M-N-O unit. Collman's proposal meant that nitrosyls could achieve coordinative unsaturation in a unique way *via* a bending of the nitrosyl group. In addition, the reverse process could be viewed as providing a driving force for the dissociation of the complexed substrate from the catalyst center at the end of the reaction sequence.[8]

To date, there have been reports of a number of nitrosyl complexes acting as catalysts for diverse reactions. These include $Rh(NO)(PPh_3)_3$ for hydrogenation,[1] $Fe(CO)_2(NO)_2$ for diene dimerization,[9] $MoCl_2(NO)_2(PPh_3)_2$ with aluminum alkyls for olefin metathesis,[10] and $MH(NO)L_3$ (M = Ru, Os; L = tertiary phosphine) for hydrogenation and isomerization.[11] The last series of complexes was synthesized by Wilson and Osborn, who also observed that for certain of the tertiary phosphines, the complexes exhibit fluxional behavior.[11] This stereochemical nonrigidity, when coupled with recent discussions of the bonding in nitrosyl complexes,[4,8,12] appears to lend support to Collman's hypothesis regarding the interconversion of nitrosyl bonding modes in catalytically active systems.

Recently there has been an upsurge of interest in polynuclear complexes as homogeneous catalysts because of their potential utility in multicenter catalyzed reactions and because of the view that such multicenter systems better

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approximate the situation encountered at metal surfaces in heterogeneous catalysis.[13-17] In 1966, Schrauzer, *et al.*,[13] reported the stereospecific dimerization of norbornadiene to "Binor-S" using $M[Co(CO)_4]$ (M = Zn, Cd, Hg) as the catalyst system. This reaction was viewed as a two-center catalyzed process. Other studies have employed carbonyl cluster compounds as catalysts, but under more extreme conditions which suggest the presence of mononuclear species. Recently, however, Chini, *et al.*,[17] have demonstrated that the hydroformylation of propene proceeds under mild consitions using $Rh_4(CO)_{12}$ in the presence of triphenylphosphine as the catalyst system. Moreover, these investigators proposed that diphenylphosphido-bridged structures are probably formed in the catalytic cycle.

In this paper we report the synthesis and characterization of two new binuclear ruthenium complexes whose structural features clearly make them candidates for more extended chemical study. These complexes possess terminally bonded nitrosyl groups, strong metal-metal bonds and diphenylphosphido bridges. The first member of this series of compounds, $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$, was discovered by the structure determination outlined below on an unexpected crystallization product from a solution of $RuH(NO)(PMePh_2)_3$ and excess phosphine. The inherent chemical interest in this binuclear complex, particularly as its structural features relate to those in catalytically active systems, stimulated us to devise a more rational synthesis of the complex and a route to other members of the series. These are described below. The general formula of complexes in this series is $[Ru(\mu\text{-}L')(NO)L]_2$ where L is a neutral two-electron donor and L′ is an anionic bridging ligand (L = $PMePh_2$ and PPh_3, and L′ = PPh_2 in the present study). Recently, an isoelectronic iridium(I)-carbonyl complex, $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$, has been reported,[18] and its structure is essentially identical with the one reported here. These binuclear complexes may thus be representative of a general class of systems which contain strong metal-metal bonds and whose electronic structures differ by two electrons from those of Roussin's red ester, $[Fe(\mu\text{-}SEt)(NO)_2]_2$,[19] and its isoelectronic analogs.[20-22]

The X-ray results presented herein have appeared in preliminary form.[23]

Experimental Section

General Methods and Materials. All reactions were carried out using a modified Schlenk apparatus with vacuum and argon (or prepurified nitrogen) sources provided *via* a double manifold. Solvents were dried and distilled under N_2 (tetrahydrofuran over $LiAlH_4$, ethanol over Mg, benzene over $LiAlH_4$). In most instances, solvents were degassed over molecular sieves (Fisher Type 4A) just prior to use. The ligands employed in the study were triphenylphosphine (Aldrich) and methyldiphenylphosphine (Strem Chemical). $RuCl_3 \cdot xH_2O$ was used as purchased from Matthey Bishop Co. The complexes $Ru(NO)Cl_3L_2$ with L = PPh_3 and $PMePh_2$ were prepared as described in the literature.[24]

Preparation of $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$. Approximately 30 ml of tetrahydrofuran (THF) was added dropwise to a Schlenk tube containing 0.05 g of Li metal, 0.63 g (1 mmol) of $Ru(NO)Cl_3(PMePh_2)_2$, and 0.79 g (3 mmol) of PPh_3 with stirring under argon. The solution became dark red-brown over a period of 1 hr. The reaction solution was filtered to remove unreacted Li and other insoluble materials, and 50 ml of anhydrous ether was added to the filtrate. The volume of the solution was reduced by pumping to approximately 30 ml and the solution was stored at 0° for several days. Dark purple crystals of the complex were then filtered and washed with methanol and ether; approximate yield 0.016 g (~10%). The ir spectrum of the crystals is identical with that of the material used in the structure determination and shows ν_{NO} of 1625 cm^{-1}. Recrystallization was accomplished using THF–methanol or THF–ether.

Anal. Calcd for $C_{50}H_{46}N_2O_2P_4Ru_2$: C, 58.25; H, 4.47. Found: C, 57.30; H, 4.17.

Preparation of $[Ru(\mu\text{-}PPh_2)(NO)(PPh_3)]_2$. Method A. A 0.27-g (1-mmol) amount of $Ru(NO)Cl_3 \cdot 2H_2O$ was dissolved in 50 ml of THF and filtered, and the filtrate was treated with 20 ml of 2,2-dimethoxypropane under argon. In a separate Schlenk tube, 0.1 g of Li metal and 1 g of PPh_3 were mixed, followed by the dropwise addition of 20 ml of THF. This solution turned gradually yellow and then deep red, indicative of $LiPPh_2$ formation.[25] The THF solution of $Ru(NO)Cl_3$ was then added to the phosphine–phosphide solution after appropriate degassing. After 30 min, 70 ml of ethanol was added, and the reaction solution was evaporated to saturation. The solution was stored in a freezer overnight. The microcrystalline product was filtered and washed with methanol and ether. The ir spectrum of the product (KBr pellet) shows ν_{NO} at 1640 cm^{-1}. Recrystallization may be accomplished using THF–methanol.

Anal. Calcd for $C_{60}H_{50}N_2O_2P_4Ru_2$: C, 62.28; H, 4.33; N, 2.42. Found: C, 61.64; H, 4.59; N, 2.40.

Method B. A 0.92-g (1-mmol) sample of $RuH(NO)(PPh_3)_3$[11] was suspended in 75 ml of decalin. The suspension was warmed to reflux giving initially a dark red-brown solution and then after *ca.* 10 min a dark purple solution. After cooling, the solution was stored in a refrigerator for 24 hr and yielded approximately 0.25 g of crude product. The ir spectrum of this material is essentially the same as that found for the product in method A.

Structure Determination of $[Ru(\mu\text{-}PPh_2)(NO)(PPh_2Me)]$

Collection and Reduction of the X-Ray Data. Crystals used in the structure determination of $[Ru(\mu\text{-}PPh_2)(NO)(PPh_2Me)]_2$ were grown over a period of several weeks from a benzene–ethanol solution of $RuH(NO)(PPh_2Me)_3$[11] to which excess phosphine had been added. In retrospect, it appears that the methyldiphenylphosphine ligand was contaminated with diphenylphosphine in order to account for the observed diphenylphosphido bridges; however, we were unable to test this hypothesis because the particular sample of the ligand had been completely expended. The syntheses described above for the binuclear systems were devised *after* the structure determination of $[Ru(\mu\text{-}PPh_2)(NO)(PPh_2Me)]_2$ had been successfully completed.

On the basis of Weissenberg and precession photographs, it was determined that the crystals belong to the monoclinic system. The observed extinctions of l odd for $h0l$ and k odd for $0k0$ uniquely determine the space group to be $P2_1/c\text{-}C_{2h}{}^5$.[26] The unit cell constants at ambient room temperature were determined from a least-squares refinement[27] of the angular settings of 20 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are found to be $a = 13.12$ (1), $b =$

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12.95 (1), $c = 15.94$ (2) Å, $\beta = 120.2$ (1)°, and $V = 2341$ Å^3. An experimental density of 1.46 (2) g/cm^3 obtained by the flotation method was in essential agreement with a calculated value of 1.47 g/cm^3 for four monomeric units of formula $C_{25}H_{23}NOP_2Ru$ or two dimers per unit cell. As a dimeric system, the complex is crystallographically required to have a center of symmetry.

A crystal of dimensions 0.55 × 0.18 × 0.17 mm, with the longest dimension parallel to the *a* axis, was mounted along the a^* axis and used for the intensity data collection. The mosaic spread of the crystal was surveyed using the narrow-source, open-counter ω-scan technique[28] and found to be satisfactory. An independent set of intensity data was collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at a takeoff angle of 1.5°. The receiving aperture was positioned 21 cm from the crystal. An unsymmetrical scan range in 2θ was used from -0.65 to $+0.75°$ of the Mo Kα peak with allowances made for the Kα_1–Kα_2 separation. The scan rate was 1°/min and 10-sec background counts were taken at each end of the scan range. The data set was collected within the angular range $5° \leqslant 2\theta \leqslant 50°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 9000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 3.0.

During data collection the intensities of four reflections in different regions of reciprocal space were monitored after every 100 measured. A significant and somewhat anisotropic decrease in the intensities of these standard reflections was noted. The final intensities of the standards averaged 78% of their original values with the largest change being observed for the 117 reflection in which the final intensity was only 71% of its initial value. The smallest intensity decrease was noted for the $02\bar{3}$ reflection with a final intensity corresponding to 87% of the original value. Plots of the intensity decrease *vs.* time were made, and the intensity data were treated upon processing with an isotropic correction corresponding to scaling an average standard up to its initial value. The observed intensity decrease was not linear with time as has been noted before.[29] In the calculations described below, the intensity data were divided into four sections and each was assigned its own variable scale factor.

The data were then processed in the usual way for Lorentz and polarization effects and reduced to a set of structure factor amplitudes F_o. The value of the linear absorption coefficient is only 8.1 cm^{-1} and no absorption correction was made. The intensities of a total of 4517 reflections were measured, of which 1659 were observed to have $F_o^2 > 3\sigma(F_o^2)$ with the estimated standard deviations σ being calculated according to the equation given below.

Solution and Refinement of the Structure. The position of the ruthenium atom was determined from a three-dimensional Patterson function. At this point it became clear that the complex we were dealing with was a centrosymmetric dimer. One cycle of least-squares refinement of the ruthenium positional and isotropic thermal parameters reduced the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ to 40.2 and 48.4%, respectively. From a succession of difference Fourier maps and least-squares refinements, the positions of all nonhydrogen atoms in the structure were determined. In these initial calculations, a preliminary, incomplete data set was employed.

The trial structure was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F_o^2)$ were estimated from counting statistics according to the formula

$$\sigma(F_o^2) = \frac{1}{Lp}[C + 0.825 + 0.25\,(t_c/t_b)^2(B_1 + B_2 + 1.65) + q^2(C^2 + (B_1 + B_2)^2)]^{1/2}$$

where Lp is the Lorentz–polarization factor, C is the total integrated count obtained in time t_c, B_1 and B_2 are the background counts each obtained in time t_b, and q is the uncertainty parameter as given by Corfield, *et al.*[30] In this structure a value of 0.04 for q was employed. The constants 0.825 and 1.65 appear in the equation because the Picker instrument truncates the least significant figure from the scaler count without proper roundoff.[31] In all calculations, the atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber[32] while the hydrogen scattering factor was taken from Stewart, *et al.*[33] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Ru and P atoms taken from the report of Cromer.[34] Throughout all refinements, the phenyl rings were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å) in the manner described previously.[30,35]

Refinement of the structure with the complete set of intensity data (1659 reflections with $F_o^2 > 3\sigma(F_o^2)$) was carried out assuming the ellipsoidal anisotropic thermal model for all individually refined nonhydrogen atoms and individual isotropic thermal parameters for the ring carbon atoms and the methyl group hydrogens. Several cycles of least-squares refinement converged to discrepancy factors R_1 and R_2 of 0.055 and 0.066, respectively, for 118 variables. In the next refinements, fixed contributions for the phenyl ring hydrogen atoms were included and this led to convergence with $R_1 = 0.054$ and $R_2 = 0.065$. Attempts were made at this stage to locate a hydride ligand originally thought to be in the ruthenium coordination sphere, but these attempts proved unsuccessful. The absence of *any* evidence indicating the presence of a hydride led us to abandon the hydride formulation and consider the refinement with $R_1 = 0.054$ as the final refinement of the structure. The largest parameter shift in this final refinement was approximately 50% of its estimated standard deviation and was for one of the methyl hydrogen positional parameters. The largest shift for the nonhydrogen parameters was approximately 15% of its estimated standard deviation. In this final refinement, 118 structural parameters were varied including four scale factors for different segments of the intensity data and 1659 reflections were used as observations in the least-squares procedure.

The parameters obtained from this refinement are taken as the final parameters for the structure and are presented in Table I along with their estimated standard deviations as obtained from the inverse matrix. The derived positional and isotropic thermal parameters for the group carbon atoms are tabulated in Table II. The estimated standard deviation of an observation of unit weight is 1.40 electrons. In Table III the root-mean-square amplitudes of thermal motion for the anisotropically refined atoms are presented. A tabulation of the final values of F_o and $|F_c|$ (in electrons × 10) for the 1659 reflections included in the refinement is available.[36]

Results

Synthetic Studies. The synthesis of the complexes $[Ru(\mu\text{-}PPh_2(NO)L]_2$ (L = PPh_3, $PMePh_2$) was devised after the structure of the methyldiphenylphosphine complex had been determined. Each synthesis is reproducible although in low yield only (<15%). In the reactions lithium serves a dual purpose. On one hand it functions as a reducing agent needed to take the Ru(II) ion of the starting material to a formal Ru(0) oxidation state in these binuclear systems, while on the other hand it reacts directly with triphenylphosphine to produce $LiPPh_2$[25] which is then incorporated as the bridging group.

Difficulties in developing syntheses for systems of the type reported herein have been and are numerous. Probably foremost among them is the introduction of the bridging group. Attempts to use $HPPh_2$ and $PClPh_2$ as sources of μ-PPh_2 as Hayter has suggested[37] have met with little success in our laboratory. Instead intractable products are obtained. The poorly systematized nature of low-valent ruthenium nitrosyl chemistry and its lack of characteristic reactions, except possibly for the return of such systems to the more stable Ru(II) starting materials, represents yet another major

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Table I. Final Positional, Thermal, and Group Parameters for $[Ru(\mu\text{-}P(C_6H_5)_2)(NO)(P(CH_3)(C_6H_5)_2)]_2$

Atomic Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
Ru	0.0886 (1)[a]	0.0642 (1)	0.0468 (1)	[b]
P1	0.0737 (3)	−0.0558 (3)	−0.0656 (2)	[b]
P2	0.2451 (3)	0.0005 (3)	0.1893 (3)	[b]
P2Me	0.2281 (21)	−0.1284 (15)	0.2222 (14)	[b]
N	0.1392 (9)	0.1862 (9)	0.0531 (7)	[b]
O	0.1676 (9)	0.2778 (8)	0.0589 (7)	[b]
MeH1	0.292 (9)	−0.147 (8)	0.284 (8)	1.2 (27)
MeH2	0.157 (10)	−0.137 (11)	0.214 (10)	2.5 (42)
MeH3	0.204 (9)	−0.174 (8)	0.170 (7)	0.9 (26)

Anisotropic Thermal Parameters

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.0069 (2)	0.0073 (1)	0.0043 (1)	0.0004 (1)	0.0030 (1)	0.0004 (1)
P1	0.0083 (4)	0.0077 (3)	0.0047 (2)	0.0012 (3)	0.0034 (2)	0.0005 (2)
P2	0.0083 (4)	0.0079 (3)	0.0046 (2)	0.0007 (3)	0.0027 (2)	0.0005 (2)
P2Me	0.0152 (28)	0.0078 (15)	0.0054 (12)	0.0012 (17)	0.0021 (16)	0.0005 (11)
N	0.0103 (12)	0.0066 (9)	0.0062 (8)	0.0025 (9)	0.0042 (8)	0.0009 (7)
O	0.0150 (13)	0.0082 (9)	0.0100 (8)	−0.0004 (9)	0.0069 (9)	0.0003 (8)

Group Parameters[d]

Group	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	−0.0600 (4)	−0.0107 (5)	0.2659 (4)	2.977 (6)	2.887 (5)	−1.470 (5)
P1R2	−0.2503 (6)	0.2498 (5)	−0.0022 (4)	−0.869 (8)	2.472 (6)	0.013 (8)
P2R1	0.3002 (5)	0.1407 (6)	0.3737 (5)	−0.347 (9)	2.494 (7)	−1.534 (8)
P2R2	0.4972 (7)	−0.0016 (5)	0.1984 (5)	−2.617 (10)	−2.401 (7)	0.685 (9)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [b] Atoms refined anisotropically. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [d] x_c, y_c, z_c are the fractional coordinates of the ring centers. The angles ϕ, θ, ρ in radians are defined in ref 12.

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms of $[Ru(\mu\text{-}P(C_6H_5)_2(NO)(P(CH_3)(C_6H_5)_2)]_2$

Group atom	x	y	z	B, Å^2
P1R1C(1)	−0.0671 (8)	0.0176 (7)	0.1789 (5)	3.9 (3)
P1R1C(2)	−0.0467 (8)	0.0923 (5)	0.2484 (7)	5.6 (3)
P1R1C(3)	−0.0396 (7)	0.0640 (7)	0.3355 (6)	6.6 (4)
P1R1C(4)	−0.0529 (8)	−0.0390 (8)	0.3530 (5)	5.7 (3)
P1R1C(5)	−0.0733 (9)	−0.1137 (5)	0.2834 (7)	6.5 (4)
P1R1C(6)	−0.0804 (7)	−0.0854 (6)	0.1964 (6)	5.1 (3)
P1R2C(1)	−0.1704 (10)	0.1682 (8)	0.0318 (8)	4.2 (3)
P1R2C(2)	−0.2740 (11)	0.1619 (6)	0.0354 (8)	7.6 (4)
P1R2C(3)	−0.3540 (7)	0.2434 (10)	0.0014 (8)	8.6 (5)
P1R2C(4)	−0.3303 (11)	0.3313 (9)	−0.0362 (9)	7.7 (4)
P1R2C(5)	−0.2267 (11)	0.3376 (6)	−0.0397 (8)	7.2 (4)
P1R2C(6)	−0.1467 (7)	0.2561 (9)	−0.0057 (7)	5.3 (3)
P2R1C(1)	0.2793 (12)	0.0784 (9)	0.2954 (7)	4.5 (3)
P2R1C(2)	0.2609 (12)	0.0398 (7)	0.3682 (9)	9.6 (5)
P2R1C(3)	0.2819 (9)	0.1021 (10)	0.4465 (7)	10.4 (6)
P2R1C(4)	0.3212 (13)	0.2030 (9)	0.4519 (7)	6.9 (4)
P2R1C(5)	0.3395 (12)	0.2416 (7)	0.3791 (9)	8.9 (5)
P2R1C(6)	0.3186 (8)	0.1793 (9)	0.3008 (7)	8.1 (4)
P2R2C(1)	0.3887 (7)	−0.0035 (13)	0.1943 (8)	4.9 (3)
P2R2C(2)	0.4037 (10)	0.0569 (10)	0.1291 (8)	9.5 (5)
P2R2C(3)	0.5121 (11)	0.0588 (9)	0.1332 (8)	12.0 (6)
P2R2C(4)	0.6057 (8)	0.0003 (14)	0.2025 (9)	7.9 (4)
P2R2C(5)	0.5907 (9)	−0.0601 (11)	0.2677 (8)	8.4 (4)
P2R2C(6)	0.4822 (9)	−0.0620 (8)	0.2636 (6)	8.2 (4)

Table III. Root-Mean-Square Amplitudes of Vibration (Å) of Anisotropically Refined Atoms[a]

Atom	Min	Intermed	Max
Ru	0.197 (2)	0.211 (3)	0.250 (2)
P(1)	0.205 (5)	0.222 (6)	0.265 (6)
P(2)	0.208 (5)	0.243 (5)	0.263 (5)
N	0.20 (2)	0.24 (1)	0.28 (2)
O	0.26 (2)	0.29 (1)	0.32 (1)
P2Me	0.22 (3)	0.26 (3)	0.36 (3)

[a] Calculated along principal axes of thermal motion.

problem in this area. Each significant departure in synthetic procedure is an excursion into the uncharted and often one is no better informed after the reaction than before.

With regard to the $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ systems, optimization of conditions or development of new reactions will eventually produce these complexes in higher yield. As noted above, Mason, *et al.*,[18] recently prepared the isoelectronic system $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$ by heating $IrH(CO)(PPh_3)_3$ in refluxing decalin. The analogous reaction using $RuH(NO)(PPh_3)_3$[11] as the starting material was then carried out in our laboratory and $[Ru(\mu\text{-}PPh_2(NO)(PPh_3)]_2$ was obtained in approximately 25% yield, representing a significant improvement. Unfortunately, the corresponding reaction starting with $RuH(NO)(PMePh_2)_3$ does not produce the hoped for product.

The nitrosyl stretching frequencies of 1625 cm^{-1} for L = $PMePh_2$ and 1640 cm^{-1} for L = PPh_3 are in the region of structural ambiguity with regard to the mode of nitrosyl bonding. For comparison, the linearly coordinated nitrosyls in $RuH(NO)L_3$ where L is a tertiary phosphine[11] have stretching frequencies in the range 1600-1640 cm^{-1} whereas ν_{NO} for the bent nitrosyls in $[RuCl(NO)_2(PPh_3)_2]^+$ [38,39] and the related complex $[Ru(OH)(NO)_2(PPh_3)_2]^+$ [40] are 1685 and 1665 cm^{-1}, respectively.

Description of the Structural Results. The crystal structure of $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ consists of the packing of discrete centrosymmetric binuclear complexes according to the parameters of Table I, the unit cell constants, and the symmetry requirements of the space group. The closest intermolecular contacts excluding hydrogens are between the nitrosyl oxygen atom and the phenyl ring carbons P2R1C(4), P2R1C(3), and P1R1C(4) (3.24, 3.25, and 3.46

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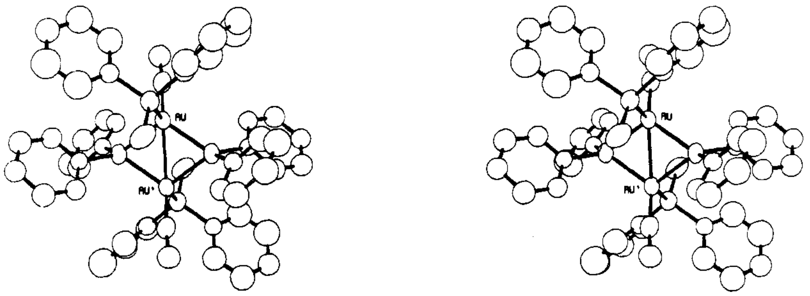

Figure 1. A stereoscopic view of the complex $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$.

Å, respectively) and between the phenyl ring carbon atoms P1R2C(3) and P2R1C(5) (3.48 Å). All other intermolecular contacts are greater than 3.58 Å and are therefore not tabulated.

The molecular structure of $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ is shown in Figure 1 and a view of the inner coordination geometry without the phosphorus substituents is presented in Figure 2. All important intramolecular distances and angles are given in Table IV. The coordination geometry about each ruthenium atom excluding the metal-metal bond is a distorted tetrahedron composed of a terminally bonded nitrosyl group, two bridging diphenylphosphido groups, and a methyldiphenylphosphine ligand. A dihedral angle of 85.6 (2)° between the planes defined by Ru, P(1), P(1)′ and Ru, P(2), N is as expected for a slightly distorted tetrahedron.

The nitrosyl group is coordinated in an essentially linear manner with a short Ru-N distance of 1.697 (12) Å and a Ru-N-O bond angle of 174.1 (10)°. The Ru-N distance is slightly but not significantly shorter than the corresponding distance in other ruthenium-linear nitrosyl complexes which is usually interpreted in terms of a strong π-back-bonding interaction between filled metal d functions and the empty π^*(NO) orbitals (1.74 (2) Å in $[Ru(NO)_2Cl(PPh_3)_2]^+$,[38] 1.74 (1) Å in $[Ru(NO)(diphos)_2]^+$,[4] 1.738 (2) Å in $[Ru(NO)Cl_5]^{2-}$,[6] 1.79 (1) Å in $RuH(NO)(PPh_3)_3$,[8] and 1.75 Å in $Ru(NO)(S_2CN(C_2H_5)_2)_3$[41]). These values are very significantly shorter than the Ru-N distance for the bent nitrosyl in $[Ru(NO)_2Cl(PPh_3)_2]^+$ [38] (1.86 (2) Å) and the Ru-N single-bond distances reported for a number of Ru(II) complexes including 2.08 (1) Å in $[Ru(py)_4(\mu\text{-}C_2O_4)Ru(py)_4]^{2+}$ [42] and 2.12 (2) Å in $[Ru(N_2)(N_3)(en)_2]^+$.[43] The N-O distance of 1.23 (1) Å is longer than most reported N-O distances in nitrosyl structures,[2,4-6,38] but little correlation seems to exist between the observed N-O bond length and the mode of nitrosyl coordination, as well as between the observed N-O bond length and ν_{N-O}, because of the relatively large estimated standard deviations usually associated with these distances (*ca.* 0.02-0.03 Å) and the nitrosyl disorder problem encountered in some of the bent and slightly bent nitrosyl structures.[5,44-47]

One of the most interesting aspects of the structure is the metal-metal bond. While the $Ru_2(\mu\text{-}P)_2$ unit is crystallographically required to be planar, the Ru-Ru distance of 2.692 (2) Å and the Ru-P(1)-Ru′ bond angle of 69.7 (1)° clearly indicates a strong metal-metal interaction. The Ru-Ru distance is significantly shorter than the 2.848-Å value found in $Ru_3(CO)_{12}$[48] and the range 2.78-2.95 Å reported for a number of substituted carbonyl cluster compounds[49-52] (an exception to this range of values is found for two of the six Ru-Ru distances in $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$ at 2.700 (5)

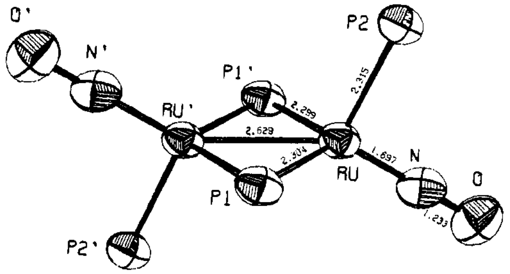

Figure 2. A perspective drawing of the inner coordination geometry of $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ in which the phosphorus substituents have been omitted for clarity.

Table IV. Important Intramolecular Distances and Angles for $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$

Distances, Å

Ru-Ru′	2.629 (2)	P(2)-P2R1C(1)	1.82 (1)
Ru-P(1)	2.304 (4)	P(2)-P2R2C(1)	1.85 (1)
Ru-P(1)′	2.299 (4)	P(1)-P1R1C(1)	1.83 (1)
Ru-P(2)	2.315 (4)	P(1)-P1R2C(1)	1.83 (1)
Ru-N	1.697 (12)	P2Me-MeH(1)	0.95 (10)
N-O	1.23 (1)	P2Me-MeH(2)	0.87 (11)
P(2)-P2Me	1.80 (2)	P2Me-MeH(3)	0.94 (10)

Angles, Deg

P(1)-Ru-P(1)′	110.3 (1)	Ru-P(2)-P2Me	116.0 (7)
P(1)-Ru-P(2)	102.0 (1)	Ru-P(2)-P2R1C(1)	113.3 (5)
P(1)-Ru-N	123.5 (4)	Ru-P(2)-P2R2C(1)	115.8 (5)
P(2)-Ru-P(1)′	106.1 (1)	P2Me-P(2)-P2R1C(1)	104.6 (9)
P(2)-Ru-N	98.4 (3)	P2Me-P(2)-P2R2C(2)	103.6 (9)
N-Ru-P(1)′	113.4 (3)	P(2)-P2Me-MeH(1)	111 (7)
Ru-N-O	174.1 (10)	P(2)-P2Me-MeH(2)	110 (10)
Ru-P(1)-Ru′	69.7 (1)	P(2)-P2Me-MeH(3)	111 (6)
Ru-P(1)-P1R1C(1)	121.8 (4)	MeH1-P2Me-MeH(2)	116 (12)
Ru-P(1)-P1R2C(1)	122.3 (4)	MeH1-P2Me-MeH(3)	120 (10)
Ru′-P(1)-P1R1C(1)	123.6 (4)	MeH2-P2Me-MeH(3)	86 (10)
Ru′-P(1)-P1R2C(1)	118.4 (4)		

Dihedral Angles between Planes, Deg

[Ru, P(1), P(1)′]-[Ru, P(2), N]	85.6 (2)
[Ru, P(1), N]-[Ru, P(1)′, P(2)]	92.3 (2)
[Ru, P(1), P(2)]-[Ru, P(1)′, N]	96.6 (2)

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and 2.717 (5) Å[53]). Perhaps a more meaningful comparison of the metal-metal distance in the present case is with the Ru-Ru bond length of 2.787 (2) Å found in the tetranuclear complex $[Ru(\mu\text{-}PPh_2)(\mu\text{-}Cl)(NO)]_4$[23] which also contains diphenylphosphido bridges between bonded Ru atoms.

A structural arrangement completely analogous to that of $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ including a short metal-metal bond has recently been reported for the isoelectronic complex $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$.[18] If conventional electron-counting methods are followed, then these systems possess formal metal-metal double bonds. In the present example, we can consider the linearly coordinated nitrosyl as a three-electron donor, the terminal phosphine as a two-electron donor, and the phosphido bridges as donating three electrons each to the two Ru atoms. This leads to 16 electrons about each Ru atom, and a double bond is therefore required to achieve the EAN configuration for the Ru atoms in this structure. While such an assignment may not be truly meaningful in terms of the chemical properties and reactivity of the system, it does underscore the strong metal-metal interaction observed.

As we have noted above, the occurrence of a binuclear complex with diphenylphosphido bridges was somewhat unexpected. The phosphido ligands are symmetrically disposed with an average Ru-P distance of 2.302 (4) Å. This value does not differ significantly from the Ru-P distance of 2.315 (4) Å for the terminal phosphine ligand. Other structures containing phosphido bridges which have been determined from single-crystal X-ray studies include $[(h^5\text{-}C_5H_5)Co(\mu\text{-}PPh_2)]_2$,[21] $[(h^5\text{-}C_5H_5)Ni(\mu\text{-}PPh_2)]_2$,[21] $[Ni(\mu\text{-}PPh_2)(CO)_2]_2$,[22] $[Mo(\mu\text{-}PMe_2)(CO)_3(PEt_3)]_2$,[54] $[Fe(\mu\text{-}PMe_2)(CO)_3I]_2$,[55] and $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$.[18] In those cases in which a metal-metal bond exists on the basis of electron counting and the M-M distance, the observed M-P-M bond angle is sharply acute and significantly reduced from the more normal, nearly tetrahedral bond angle found in the other systems. In general the M-X-M bond angle where X is a bridging three-electron donor unit (PR_2, SR, Cl, etc.) has been used, most notably by Dahl and coworkers,[20] to estimate the existence of metal-metal bonding. Clearly the interaction in the present case is a strong one. The Ru-P-Ru bond angle of 69.7 (1)° is among the smallest known for M-X-M values.

An additional and closely related feature of the bridging structure is that the Ru-bridging P bonds are somewhat shorter than expected (one might have expected the Ru-bridging P distance to be longer than the Ru-terminal P distance). In addition, these Ru-P distances are shorter than the corresponding values in other reported ruthenium phosphine nitrosyls.[4,8,38,56] One possible rationalization of the observed structural results for $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$ and its isoelectronic analog $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$ is that π-back-bonding is much more important for diphenylphosphido bridges than for other bridging units as proposed by Dahl, *et al.*[21] An alternative view for systems of this type in which the M_2X_2 bridge is essentially planar is that a short M-M bond length without a shortened M-X bond length would result in even greater angle strain at the bridging X atoms. These factors probably reinforce each other in the present case.

Discussion

The binuclear complexes $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ with L = PPh_3 and $PMePh_2$ reported herein and the isoelectronic system $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$ represent a new class of binuclear complexes. In their electronic structures, these systems have two less electrons in the metal valence orbitals than do the structurally similar compounds $[Fe(\mu\text{-}SEt)(NO)_2]_2$,[19] $[Ni(\mu\text{-}PPh_2)(CO)_2]_2$,[22] and $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$[57] which also possess metal-metal bonds. A double bond is therefore postulated for the M-M bond order in the present systems in order to satisfy the EAN rule and account for the diamagnetism of these complexes. It is therefore tempting to propose that the highest filled orbital in systems such as $[Fe(\mu\text{-}SR)(NO)_2]_2$ is a π^* orbital of the metal-metal bond although such an extrapolation of results may be a bit tenuous at this time.

In the course of studying the systems $[Ru(\mu\text{-}PPh_2)(NO)L]_2$, we considered an alternative formulation of the complexes as hydrides. This formulation as $[RuH(\mu\text{-}PPh_2)(NO)L]_2$ does not require the postulated Ru-Ru double bond and it has certain points of appeal. However, nmr and infrared spectroscopic data have shown no evidence for the presence of a hydride, and this formulation is therefore eliminated.

Chemically, the binuclear nitrosyls are intriguing. The metal-metal interaction is strong, as has been noted above, but it may also be susceptible to attack. Cleavage of the M-M bond in such systems would yield coordinatively unsaturated metal ions. This coordinative unsaturation could also be achieved by a bending of the nitrosyl ligand or by a dissociation of the tertiary phosphine ligand. In addition, the proximity of the two metal ions in these systems may make bicentered catalysis possible. In order to enhance this possibility, we are investigating systems in which the bridging ligands are far less imposing sterically so that the metal centers are more accessible to binding substrates and activating molecules. Preliminary studies in our laboratory[58] have shown that the system $[Ru(\mu\text{-}PPh_2)(NO)L]_2$ does not function as a hydrogenation catalyst following previously published procedures.[59] Other assays for catalytic activity are being explored.

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Registry No. $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$, 39045-39-1; $[Ru(\mu\text{-}PPh_2)(NO)(PPh_3)]_2$, 41666-87-9; $Ru(NO)Cl_3(PMePh_2)_2$, 15392-52-6; PPh_3, 603-35-0; $Ru(NO)Cl_3$, 18902-42-6; $RuH(NO)(PPh_3)_3$, 33991-11-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× re-

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Palladium(0) Complexes of Dibenzylideneacetone. Formation and Molecular Structure of Tris(dibenzylideneacetone)palladium(0)

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The complex $Pd(C_{17}OH_{14})_3$ has been prepared and isolated as the benzene solvate. From three-dimensional X-ray data collected by the θ-2θ scan technique the crystal and molecular structure of the complex has been determined. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional R factor of 0.084 for 2449 nonzero reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 13.684$ (5) Å, $b = 15.938$ (5) Å, $c = 16.094$ (5) Å, $\alpha = 122.92$ (5)°, $\beta = 127.45$ (5)°, $\lambda = 63.82$ (5)°, and $V = 2307$ Å^3. There are two formula weights per unit cell ($\rho_{\text{exptl}} = 1.26$ (1) g/cm^3; $\rho_{\text{calcd}} = 1.276$ g/cm^3). Each pentadienone ligand is coordinated to the metal through one olefin group. The coordination geometry about the Pd atom is essentially trigonal with the molecule having approximate C_3 symmetry.

Introduction

Organopalladium complexes have been of interest as homogeneous catalysts and models for catalytic reactions. A review of organopalladium chemistry, however, will reveal that practically all work in this area has been performed on complexes of Pd(II).[1] This appears to be related to the scarcity of Pd(0) organometallic complexes and the relative instability of those which are known. Few reports have appeared on Pd(0)-olefin complexes in contrast to the great interest in Ni(0)- and Pt(0)-olefin complexes and their use as catalytic agents. Attempts to prepare the bis(1,5-cyclooctadiene) complex of Pd(0) using procedures found to be successful for similar Ni(0) and Pt(0) compounds have failed.[2] The ethylene complex $Pd(P(C_6H_5)_3)_2(C_2H_4)$ has been reported but appears to be less stable than the Ni or Pt analogs.[3] These results may be interpreted in terms of the view that Pd(0) has a much lower affinity for olefin coordination than Ni or Pt.[4]

Recently Takahashi, *et al.*, noted that addition of sodium acetate to a solution of $PdCl_4^{2-}$ and dibenzylideneacetone (DBA) (1,5-diphenyl-3-pentadienone) gave the complex $Pd(DBA)_2$.[5] Subsequent reports by Maitlis have extended this work to Pt and have indicated that these compounds may be useful as alkyne oligomerization catalysts.[6] Additionally, the absence of ^{195}Pt coupling to olefin protons in the nmr of $Pt(DBA)_2$ has been interpreted to indicate DBA coordination through carbonyl groups.

We have noted previously that $Pd(DBA)_2$ dissociates in solution giving the binuclear complex $Pd_2(DBA)_3$.[7] The metal atoms in this molecule have trigonal coordination geometries with the pentadienone ligands bridging and bonding through olefin groups. We wish to report herein the formation of the complex $Pd(DBA)_3$ by addition of excess DBA to $Pd(DBA)_2$, thus indicating the existence of the reversible series of Pd-DBA complexes

$$Pd_2(DBA)_3 \overset{DBA}{\rightleftharpoons} Pd(DBA)_2 \overset{DBA}{\rightleftharpoons} Pd(DBA)_3$$

Synthesis and Properties of the Complex

A fourfold excess of dibenzylideneacetone was added to a benzene solution of $Pd(DBA)_2$.[8] The solution was heated and reduced in volume. The color gradually changed from the dark red of $Pd(DBA)_2$ to dark brown. For the present study the solution was allowed to evaporate entirely giving orange-brown crystals of $Pd(DBA)_3$ among yellow crystals of DBA. An elemental analysis of the complex indicated the presence of one benzene solvate molecule per molecule of complex. The complex $Pd(DBA)_3$ readily dissociates in solution in the absence of excess DBA giving $Pd(DBA)_2$. Attempts to wash crystals isolated in this way resulted in loss of the benzene solvate and crystal decomposition. The infrared spectrum of the complex shows a band predominantly ν(C=O) at 1651 cm^{-1}, with olefin bands at 1598, 1580, and 1531 cm^{-1}.

Collection and Reduction of the X-Ray Data

A crystal of the complex $Pd(DBA)_3 \cdot C_6H_6$ was isolated and prepared for the crystallographic study. The crystal was coated with an amorphous resin to retard loss of the benzene solvate. On the basis of Weissenberg and precession photographs of the *hk*0, *hk*1, *h*0*l*, *h*1*l*, 0*kl*, and 1*kl* zones it was established that the complex crystallizes in the triclinic system. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 20 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 13.684$ (5) Å, $b = 15.938$ (5) Å, $c = 16.094$ (5) Å, $\alpha = 122.92$ (5)°, $\beta = 127.45$ (5)°, $\gamma = 63.82$ (5)°, and $V = 2307$ Å^3. An experimental density of 1.26 (1) g/cm^3 obtained by the flotation method agrees with a calculated value of 1.276 g/cm^3 for two $Pd(C_{17}OH_{14})_3 \cdot C_6H_6$ formula weights per unit cell. Space group $P\bar{1}$ (C_i^1, No. 2)[9] was chosen for the refinement. A crystal of dimensions 0.21 × 0.23 × 0.35 mm was mounted along the a^* axis and prepared for data collection. The mosaic spread of the crystal was determined

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