

2962, 2930, 2870, 2920, 1095, 1080, 1070 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{NO}$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.93; H, 11.69; N, 7.68.

The amination in the presence of AgBF_4 was done by using the same procedure as described above. In this case AgBF_4 (195 mg, 1 mmol) in THF (1 mL) was added immediately after the addition of triphenylphosphine. The isomeric amines 3, 4, and 5 were separated by preparative GLC. In the amination with dimethylamine the amine was added by using a 2.5 M solution in THF.

Spectral Data for Amines 2, 4, and 5. 2: NMR (CDCl_3) δ 6.0-5.8 (m, 2, $\text{CH}=\text{CH}$), 3.64 (m, 1, CHO), 3.36 (s, 3, OMe), 3.09 (m, 1, CHN), 2.30 (s, 6, NMe_2), 1.7-1.5 (m, 4, CH_2CH_2).

4: NMR (CDCl_3) δ 5.85 (m, 1, $=\text{CH}$), 5.75 (m, 1, $=\text{CH}$), 3.84 (m, 1, CHO), 3.46 (m, 1, CHN), 3.36 (s, 3, OMe), 2.53 (q, 2, NCH_2), 2.45 (q, 2, NCH_2), 1.8-1.4 (m, 4, CH_2CH_2), 1.05 (t, $J = 7.5$ Hz, 6, CCH_3).

5: NMR (CDCl_3) δ 5.78 (m, 1, $=\text{CH}$), 5.54 (m, 1, $=\text{CH}$), 3.43 (s, 3, MeO), 3.34 (m, 2, CHO and CHN), 2.60 (q, 4, NCH_2), 2.1-1.9 (m, 4, CH_2CH_2), 1.06 (t, $J = 7.3$ Hz, 3, CCH_3).

Carbonylation of 1 in the Presence of Diethylamine. To a stirred solution of 1 (50 mg, 0.2 mmol of palladium) in THF at room temperature was added diethylamine (156 μL , 1.5 mmol)

followed by bubbling carbon monoxide through the solution. After a few minutes palladium zero precipitated. After 3 h the conversion was complete (by GLC) and 0.5 mL of 2 M NaOH and 2 mL of ether were added. After filtration, the organic layer was separated and the aqueous phase was extracted with ether. The combined organic phase was washed with saturated NaCl(aq) and dried (MgSO_4). Evaporation of the solvent gave 20 mg of crude amide 6. The product was purified by preparative TLC (silica gel, EtOAc/hexane, 1:1): R_f (TLC) 0.3; yield 20%; NMR (CDCl_3) δ 5.79 (m, 1, $=\text{CH}$), 5.34 (m, 1, $=\text{CH}$), 3.78 (ddd, $J = 10.8, 7.7$, and 3.1 Hz, 1, CHO), 3.6-3.3 (m, 5, NCH_2 and CHCO), 3.36 (s, 3, MeO), 2.3-2.1 (m, 2, CH_2), 1.7-1.4 (m, 2, CH_2) 1.22 (t, $J = 7.1$ Hz, 3, CCH_3), 1.13 (t, $J = 7.1$ Hz, 3, CCH_3); mass spectrum, m/e (relative intensity), 211 (M^+ , 8), 196 (14), 107 (15), 100 (100), 81 (22), 78 (31), 77 (16), 72 (84), 53 (18), 44 (26).

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Synthesis and X-ray Crystal Structures of $[\text{M}(\mu\text{-}(t\text{-Bu})(\text{H})\text{P})(\text{PMe}_3)_2]_2$ (M = Rh, Ni) Containing Rh=Rh Double and Ni-Ni Single Bonds

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The isostructural, dinuclear complexes $[\text{M}(\mu\text{-}(t\text{-Bu})(\text{H})\text{P})(\text{PMe}_3)_2]_2$, M = Rh (1) and Ni (2), have been synthesized and characterized and their structures determined by X-ray diffraction studies. 1 can be isolated from the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with $\text{Li}_2\text{P-}t\text{-Bu}$ in THF after treatment with excess PMe_3 . 2 is formed from the reaction of $\text{NiCl}_2(\text{PMe}_3)_2$ and $\text{Li}_2\text{P-}t\text{-Bu}$ in THF. The X-ray structures of 1 and 2 show two metal atoms, each bonded to two terminal PMe_3 ligands and bridged by two *tert*-butylphosphido ($(t\text{-Bu})(\text{H})\text{P}^-$) groups. The metal-metal distances and electron counts indicate the presence of double and single metal-metal bonds in 1 and 2, respectively (Rh-Rh = 2.552 (2) Å and Ni-Ni = 2.559 (2) Å). The coordination geometry about each metal is distorted tetrahedral (ignoring the metal-metal interaction). Crystal data for 1: monoclinic, space group $C2/m$ (No. 12), $a = 17.495$ (11) Å, $b = 11.913$ (2) Å, $c = 8.815$ (3) Å, $\beta = 115.11$ (4)°, $U = 1664$ (3) Å³, $Z = 2$, $D_{\text{calcd}} = 1.37$ g cm^{-3} , $\lambda(\text{Mo K}\alpha)$ (graphite monochromator) = 0.71069 Å, $\mu(\text{Mo K}\alpha) = 11.60$ cm^{-1} , $T = 298$ K. Refinement with 792 observed (1729 measured) reflections gave a final $R = 0.044$ and $R_w = 0.049$. Crystal data for 2: monoclinic, space group $C2/m$ (No. 12), $a = 17.871$ (8) Å, $b = 11.643$ (7) Å, $c = 8.833$ (4) Å, $\beta = 116.44$ (3)°, $U = 1646$ (3) Å³, $Z = 2$, $D_{\text{calcd}} = 1.21$ g cm^{-3} , $\lambda(\text{Mo K}\alpha)$ (graphite monochromator) = 0.71069 Å, $\mu(\text{Mo K}\alpha) = 14.44$ cm^{-1} , $T = 298$ K. Refinement with 1059 observed (1158 measured) reflections gave $R_1 = 0.0605$ and $R_w = 0.0655$.

Introduction

There is growing interest in the chemistry of phosphido (R_2P^-) complexes of transition metals since these types of ligands can act as versatile bridging units between two or more metal centers. We have initiated a broad program aimed at the study of steric and electronic effects involved in these types of compounds. Our initial studies have focused on the use of the bulky di-*tert*-butylphosphido ($t\text{-Bu}_2\text{P}^-$) group.¹⁻⁵ We report here the synthesis and

structures of two isostructural complexes of Rh(I) and Ni(I) in which the two metal atoms are bridged by the sterically less demanding *tert*-butylphosphido ($(t\text{-Bu})(\text{H})\text{P}^-$) group.

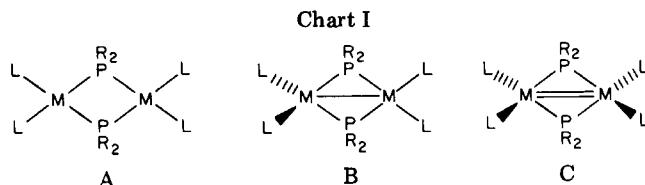
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M = Co, Rh, Ir; L = two-electron donor, CO, PR₃, N₃, etc.

For rhodium, a number of diphenylphosphido-bridged complexes have recently been reported. These include Rh₃ and Rh₄ clusters such as Rh₃(μ-PPh₂)₃(CO)₃(PPh₃)₂,⁶ Rh₃(μ-PPh₂)₃(CO)₅,⁷ Rh₄(μ-PPh₂)₄(CO)₅(PPh₃),⁸ and [Rh₄(CO)₅(μ-PPh₂)₅]⁻⁹. Also a series of dinuclear complexes has recently been prepared by Meek and co-workers.⁹⁻¹²

Using the bulky *t*-Bu₂P⁻ ligand we have so far reported the synthesis and characterization of the trimer [Rh(μ-*t*-Bu₂P)CO]₃² and two isomers of the dinuclear complex [Rh(μ-*t*-Bu₂P)(CO)₂]₂.³ This latter system exhibits the unusual feature of a reversible formation and cleavage of a metal-metal bond accompanied only by a geometrical isomerism.

For diphosphido-bridged dimers of the cobalt group that have, in general, two terminal two-electron donors (L) or a chelating four-electron donor such as a diphosphine or diolefin three types of geometrical isomers (A-C) have been observed (see Chart I). The key point of interest is that the three isomers A, B, and C have metal-metal bonds of order 0, 1, and 2, respectively. In most cases the central M₂P₂ cores are planar (either crystallographically imposed or "planar" within experimental error). Thus the metal-metal bond orders may be correlated with the geometries adopted by the terminal ligands (L).

In A the terminal groups give each metal atom a planar environment ("planar/planar") and there is no metal-metal bond. Examples of this type of complex include one isomer of [Rh(μ-*t*-Bu₂P)(CO)₂]₂,³ [Rh(μ-P(CH₂CMe₃)₂)(CO)₂]₂,¹³ and [Rh(μ-PPh₂)(Ph₂PCH₂CH₂PPh₂)₂]₂.¹² Although in the latter example there is considerable distortion from planarity in the central Rh₂P₂ core (dihedral angle of 133.4 (4)°). For B the terminal ligands give one metal a planar environment and the other a distorted tetrahedral geometry ("planar/tetrahedral") and the metal-metal distances suggest a single bond. Examples include Rh₂(μ-PPh₂)₂(PET₃)₂(COD)¹⁰ and another isomer of [Rh(μ-*t*-Bu₂P)(CO)₂]₂.³ For isomer C the two metals have distorted tetrahedral geometries and a metal-metal bond of order 2 is observed. Examples include [Co(μ-PPh₂)(CO)(PET₂Ph)]₂,¹⁴ [Co(μ-*t*-Bu₂P)(CO)N₂]₂,⁵ and [Ir(μ-PPh₂)(CO)(PPh₃)₂]₂.¹⁵ Studies by Hoffmann and

Summerville on geometries A and C suggest that any d₈ four-coordinate dimer such as [Rh(μ-PR₂)(CO)₂]₂ will be "tetrahedral/tetrahedral" (i.e., type C) if the bridging ligands are not π donors and this geometry best favors metal-metal bonding.¹⁶

The dinuclear rhodium complex [Rh(μ-(*t*-Bu)(H)P)(PMe₃)₂]₂ (1) described in this paper does have a geometry best represented by C and contains a Rh=Rh double bond that is relatively rare in dirhodium chemistry.¹⁷ The isostructural nickel complex 2 requires only a single metal-metal bond in order for the nickel atoms to achieve 18-electron configurations. The structure of 2 is therefore similar to [Ni(μ-Ph₂P)(CO)₂]₂¹⁸ although there are significant distortions in the structure due to the asymmetric nature of the μ-(*t*-Bu)(H)P ligand.

A reasonable number of (alkyl)(H)P⁻ phosphido complexes are known although they are not as common as dialkyl- or diarylphosphides (R₂P⁻).¹⁹

Results

The reaction of [Rh(COD)Cl]₂ (COD = 1,5-cyclooctadiene) with 1 equiv of Li₂-*t*-BuP in THF at -100 °C yields a dark red-purple solution. Although we were unable to isolate a pure compound from this solution treatment with excess PMe₃ permits the isolation of [Rh(μ-(*t*-Bu)(H)P)(PMe₃)₂]₂ (1), as bright red hexane-soluble crystals in high yield. The presence of hydrogen in the μ-(*t*-Bu)(H)P groups could be due to proton abstraction from THF solvent although at present we have no data to support this.

Spectroscopic data for 1 are in accord with the structure as determined by X-ray diffraction. The IR spectrum shows ν_{P-H} = 2140 (m) cm⁻¹ while the ³¹P{¹H} NMR shows two well-resolved resonances. One is shifted downfield at δ 207.25 (relative to 85% H₃PO₄) and assigned to the bridging phosphorus nuclei. The other comes in a position expected for Rh(I)-PMe₃ resonances.²⁰ Large downfield shifts have also been observed in many diphenylphosphido-bridged dinuclear systems in which the metals are separated by bonding distances.⁶⁻¹¹ The spectrum is temperature independent from -80 to +50 °C, and both Rh-P and P-P couplings are well resolved. We have had some success at simulation of this A₂A₂'M₂X₂ spin system (see Experimental Section). The phosphido resonance appears to consist of a triplet of pentuplets (¹J_{Rh-P} = 150.9 Hz, ²J_{P-P} = 17.2 Hz) while the PMe₃ resonance appears as a doublet of triplets with a complex pattern of lines of less intensity between the overall doublet structure (J_{Rh-P} = 156.8 Hz). Several other phosphido-bridged dimers of the cobalt triad containing terminal phosphine ligands and with pseudotetrahedral metals are known in which virtually no phosphorus-phosphorus coupling is observed.^{5,11,14} In contrast in the "planar/planar" arrangement significant P-P coupling is found. Although 1 and 2 are best described as "tetrahedral/tetrahedral" (form C) the structures show some distortion toward the "planar/planar"

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1 and 2

	$C_{20}H_{56}P_6Rh_2$ (1)	$C_{20}H_{56}P_6Ni_2$ (2)
mol wt	688.32	599.93
space group	$C2/m$ (No. 12)	$C2/m$ (No. 12)
cell constants		
a , Å	17.495 (11)	17.871 (8)
b , Å	11.913 (3)	11.643 (7)
c , Å	8.815 (3)	8.833 (4)
β , deg	115.11 (4)	116.44 (3)
cell vol, Å ³	1664 (3)	1646 (3)
molecules/unit cell	2	2
D_{calcd} , g cm ⁻³	1.37	1.09
μ (calcd), cm ⁻¹	11.60	14.44
radiation, Å	Mo K α , 0.710 69	Mo K α , 0.710 69
max cryst dimens, mm	0.40 × 0.20 × 0.20	0.35 × 0.20 × 0.20
std reflcns	660, $\bar{6}60$, $\bar{6}60$	201, 400
decay of stds	< 4%	< 2%
reflctns measd	1729	1158
2θ range, deg	2-40	3-45
reflctns obsd ($I > 3\sigma(I)$)	792	1059
no. of parameters varied	71	72
R	0.044	0.0605
R_w	0.049	0.0655

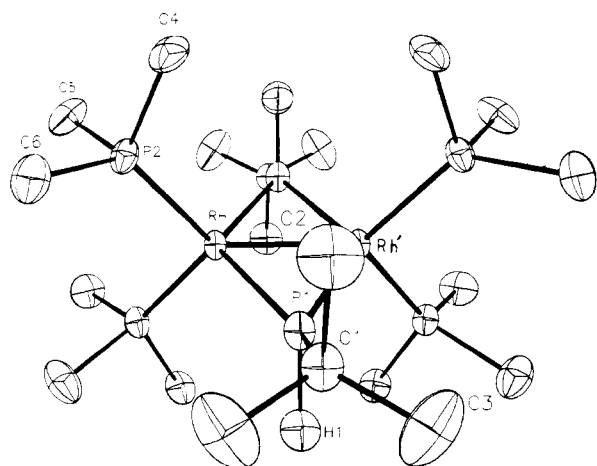


Figure 1. A general view of 1. Key bond lengths and angles are listed in Table III.

form. Thus, the fact that P-P coupling is observed in 1 may be taken as evidence for the solution structure being the same in the solid state, the perturbation toward planarity accounting for observed J_{P-P} values.

The lack of P-P coupling in the "tetrahedral/tetrahedral" case is presumably a result of different sets of metal orbitals being used to bond to the $\mu-(t-Bu)(H)P$ and PMe_3 groups while in the "planar/planar" examples common sets of orbitals are used in both bridging and terminal metal-phosphorus bonding.

The resonance Raman spectrum of 1 in hexane solution at 25 °C shows a medium intensity absorption at 168 cm⁻¹ which we tentatively assign to the Rh=Rh stretch. Other stretches for single Rh-Rh bonds come in the region of ca. 150 cm⁻¹.²¹

X-ray Structure of 1. In the solid state 1 exists as isolated neutral molecules with no short intermolecular contacts. (Crystal data and the summary of intensity data collection parameters for both 1 and 2 are given in Table

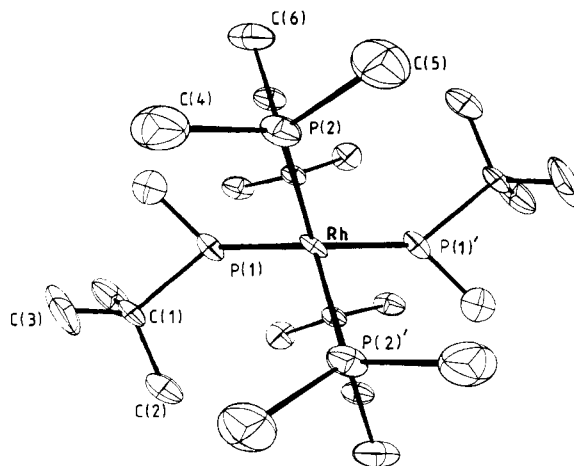
Figure 2. A view of 1 down the Rh-Rh vector showing the alignment of PMe_3 groups.

Table II. Positional Parameters for 1

atom	x/a	y/b	z/c
Rh	0.5000	0.10719 (9)	0.0000
P(1)	0.5825 (2)	0.0000	0.2256 (5)
C(1)	0.7005 (8)	0.0000	0.353 (2)
C(2)	0.740 (1)	0.0000	0.230 (2)
C(3)	0.7253 (7)	-0.104 (1)	0.452 (2)
P(2)	0.5551 (2)	0.2316 (2)	-0.1164 (3)
C(4)	0.6068 (7)	0.166 (1)	-0.233 (1)
C(5)	0.4863 (8)	0.329 (1)	-0.277 (2)
C(6)	0.6373 (8)	0.330 (1)	0.014 (2)
H(1)	0.58 (1)	0.0000	0.40 (1)
H(2)	0.781 (1)	0.0000	0.308 (2)
H(3)	0.727 (1)	0.069 (2)	0.161 (2)
H(4)	0.7052 (7)	-0.115 (1)	0.545 (2)
H(5)	0.7887 (7)	-0.093 (1)	0.511 (2)
H(6)	0.7141 (7)	-0.177 (1)	0.387 (2)
H(7)	0.6516 (7)	0.121 (1)	-0.145 (1)
H(8)	0.6339 (7)	0.224 (1)	-0.278 (1)
H(9)	0.5709 (7)	0.115 (1)	-0.328 (1)
H(10)	0.4610 (8)	0.373 (1)	-0.213 (2)
H(11)	0.4405 (8)	0.287 (1)	-0.369 (2)
H(12)	0.5145 (8)	0.381 (1)	-0.326 (2)
H(13)	0.6843 (8)	0.280 (1)	0.088 (2)
H(14)	0.6257 (8)	0.387 (1)	0.089 (2)
H(15)	0.6531 (8)	0.372 (1)	-0.065 (2)

I.) A general view of 1 is shown in Figure 1. Each rhodium atom is bonded to two terminal PMe_3 ligands ($Rh-P(2) = 2.239$ (3) Å) and two bridging phosphido groups ($Rh-P(1) = 2.286$ (3) Å) and has a distorted tetrahedral coordination geometry. The Rh-Rh bond length of 2.552 (2) Å is consistent with a formal double bond required for two 18-electron rhodium atoms rather than the absence of a bond required for two 16-electron metal centers. Each dimer resides on a crystallographic center of inversion formed by a twofold axis passing through the two rhodium atoms and a mirror plane containing the bridging phosphorus atoms and which is perpendicular to the Rh-Rh vector. The crystallographic symmetry ($2/m$) imposed on the structure therefore requires two completely symmetrical and planar Rh-P(1)-Rh' bridges similar to those found in other systems.¹⁻⁵ One feature of the structure deserves special comment. As shown in Figure 2, which is a view along the Rh-Rh vector, the planes Rh-Rh'-P(1)-P(1)' and Rh-Rh'-P(2)-P(2)' are not perpendicular to each other, unlike the situation found with other "tetrahedral/tetrahedral" phosphido-bridged rhodium dimers where the two substituents on the phosphido bridge are identical.²² The angle between these planes

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Table III. Bond Lengths (Å) and Angles (deg) for 1

Bond Distances					
Rh-Rh	2.552 (2)	C(1)-C(2)	1.52 (2)	P(2)-C(4)	1.81 (1)
Rh-P(2)	2.239 (3)	Rh-P(1)	2.286 (3)	P(2)-C(6)	1.83 (1)
P(1)-H(1)	1.6 (1)	P(1)-C(1)	1.88 (1)	C(1)-C(3)	1.47 (1)
P(2)-C(5)	1.83 (1)				
Bond Angles					
P(1)-Rh-P(1)'	112.14 (8)	P(1)-C(1)-C(2)	107 (1)	C(1)-P(1)-H(1)	84 (8)
P(1)-Rh-P(2)	122.1 (1)	P(1)-C(1)-C(3)	109.1 (8)	Rh-P(2)-C(5)	120.3 (4)
Rh-P(1)-Rh'	67.9 (1)	P(1)-Rh-P(2)	101.9 (1)	Rh-P(2)-C(6)	120.7 (4)
Rh-P(1)-H(1)	126 (6)	P(2)-Rh-P(2)'	97.2 (1)	C(5)-P(2)-C(6)	99.5 (6)
Rh-P(2)-C(4)	113.1 (4)	Rh-P(1)-C(1)	130.3 (3)	C(3)-C(1)-C(3)'	115 (1)
C(4)-P(2)-C(5)	99.0 (5)			C(2)-C(1)-C(3)	108.4 (9)
C(4)-P(2)-C(6)	100.5 (6)				

Table IV. Atom Coordinates ($\times 10^2$) and Temperature Factors ($10^2 \times A^2$) for 2

atom	x	y	z	U(iso) ^a
Ni	0	1099 (1)	0	34 (1)
P(1)	793 (1)	0	2087 (2)	41 (1)
P(2)	588 (1)	2208 (1)	-1150 (2)	50 (1)
C(1)	1965 (5)	0	3339 (10)	50 (3)
C(2)	2357 (5)	0	2097 (13)	71 (5)
C(3)	2237 (4)	1070 (7)	4427 (10)	85 (4)
C(4)	1065 (4)	1604 (6)	-2416 (9)	72 (3)
C(5)	-114 (5)	3219 (7)	-2724 (10)	87 (4)
C(6)	1411 (4)	3204 (7)	178 (10)	87 (4)

^a Equivalent isotropic U defined as one-third of the trace-orthogonalized U tensor.

is 105.2 (1)°. The two substituents on the bridging phosphido group are vastly different in size (*t*-Bu vs. H) so presumably the twist of 15.2 (1)° occurs in order to relieve the steric strain between the P-*t*-Bu and PMe₃ groups. Atomic positional parameters for 1 are given in Table II and bond lengths and angles in Table III. The thermal parameters and structure factors are available as supplementary material.²³

Nickel. The reaction of NiCl₂(PMe₃)₂ with one equivalent of Li₂P-*t*-Bu in THF at -10 °C rapidly yields a reddish brown solution from which [Ni(μ-*t*-Bu)(H)P-(PMe₃)₂]₂ (2) may be isolated in high yield (80%). This complex has an intense purple color in hydrocarbon solutions and is readily recrystallized from hexane. As with the rhodium analogue the P-H units of the μ-*t*-Bu)(H)P groups are evident in the IR spectrum ($\nu_{\text{P-H}} = 2160$ (m) cm⁻¹). However, unlike 1, ³¹P{¹H} NMR data for this complex over a range of temperatures and in several solvents give no structural information. In toluene-*d*₆ at room temperature four broad single resonances are observed at δ 160.00, 136.54, -22.13, and -32.00 (relative to 85% H₃PO₄). There is virtually no change in the spectrum from -80 to +50 °C. Although the two resonances to low field (δ 160.00 and 136.54) can be assigned to the μ-*t*-Bu)(H)P groups, no P-P coupling constant information can be obtained. The reason for the different spectra in 1 and 2 is not clear at present. Phosphine exchange processes could occur for 2 in solution that would destroy P-P coupling. In the presence of excess PMe₃ the phosphine groups of 2 are labile. The ³¹P{¹H} NMR spectrum now consists of two single slightly broadened resonances at room temperature (δ 131.7 (μ-*t*-Bu)(H)P) and -20.2 (PMe₃), and 2 can be recovered unchanged from the solution.

X-ray Structure of 2. The structure of 2 differs in no fundamental manner from that of 1. A view of the molecule is shown in Figure 3. Atomic positional parameters and bond lengths and angles are given in Tables IV and

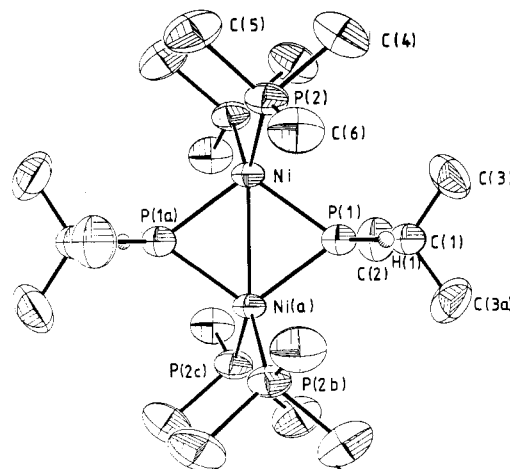


Figure 3. A general view of 3. Key bond lengths and angles are listed in Table V.

V respectively. The Ni-P(phosphido) distance Ni-P(1) is 2.172 (1) Å, and the Ni-PMe₃ length Ni-P(2) is 2.181 (2) Å. The unique angles about each pseudotetrahedral nickel(I) are P(2)-Ni-P(1) = 118.4°, P(2)-Ni-P(2a) = 107.4 (1)°, P(1)-Ni-P(1a) = 107.8°, and P(1)-Ni-P(2a) = 102.8 (1)°. The Ni-Ni distance of 2.559 (2) Å can be compared with that in [Ni(μ-Ph₂P)(CO)₂]₂¹⁸ (2.51 Å) and indicates a single bond. Treating the phosphido groups as three electron donors each nickel satisfies the 18-electron rule. One may also compare the Ni-Ni distance in 2 with that found in [Ni(μ-*t*-Bu₂P)(PMe₃)₂]₂ (2.559 (2) vs. 2.375 (3) Å, respectively). Two factors may be responsible for this difference. The formal electron counts for each Ni(I) atom are 18 and 16 in 2 and [(Ni(μ-*t*-Bu₂P)(PMe₃)₂]₂, respectively. One would expect a single Ni-Ni bond between two 16-electron Ni(I) atoms to be shorter than that for two 18-electron atoms. Also in 2 each Ni atom bears two PMe₃ ligands as opposed to one for [Ni(μ-*t*-Bu₂P)(PMe₃)₂]₂. Steric factors may therefore be partly responsible for the increased Ni-Ni separation in 2. As found for 1 the central Ni-Ni(a)-P(1)-P(1a) plane is tilted with respect to that which contains the four PMe₃ groups and the nickel atoms (Ni-Ni(a)-P(2)-P(2a)-P(2b)-P(2c)). The angle between the two planes in this case is 101.3 (1)° which is notably smaller by 3.9° than that found in 1 (Figure 4). One possible explanation for this difference can be found not in the metal-metal separations since they are almost the same (Rh-Rh = 2.552 (2) Å and Ni-Ni = 2.559 (2) Å), but in the increased metal-phosphorus bond lengths in the rhodium complex. The covalent radii are 1.25 and 1.15 Å for Rh and Ni, respectively. Thus both the M-P(phosphido) and M-P(PMe₃) bond lengths are longer in the Rh complex by 0.058 (3) and 0.114 (2) Å, respectively. Thus the phosphorus-phosphorus separations are greater for 1 which allows a greater twist in order to relieve steric

(23) See paragraph at end of paper regarding supplementary material.

Table V. Bond Lengths (Å) and Angles (deg) for 2

Bond Distances					
Ni-P(1)	2.172 (1)	Ni(a)-P(1a)	2.172 (1)	P(2)-C(4)	1.822 (9)
Ni-Ni(a)	2.559 (2)	P(2a)-Ni	2.181 (2)	P(2)-C(6)	1.830 (7)
Ni-P(2a)	2.181 (2)	P(1)-H(1)	1.440 (93)	C(1)-C(3)	1.515 (9)
P(1)-Ni(a)	2.172 (1)	Ni-P(2)	2.181 (2)	Ni(a)-P(1)	2.172 (1)
P(2)-C(5)	1.828 (7)	Ni-P(1a)	2.172 (1)	P(1a)-Ni(a)	2.172 (1)
C(1)-C(2)	1.542 (17)	P(1)-C(1)	1.883 (8)	C(3a)-C(1)	1.515 (9)
C(1)-C(3a)	1.515 (9)				
Bond Angles					
P(1)-Ni-P(2)	118.4 (1)	P(1)-C(1)-C(3a)	109.4 (5)	Ni-P(1)-Ni(a)	72.2 (1)
P(2)-Ni-Ni(a)	126.3	C(3)-C(1)-C(3a)	110.6 (7)	Ni-P(2)-C(4)	120.8 (3)
P(2)-Ni-P(1a)	102.8 (1)	Ni-Ni(a)-P(1a)	53.9	C(4)-P(2)-C(5)	97.6 (4)
P(1)-Ni-P(2a)	102.8 (1)	Ni-P(1a)-Ni(a)	72.2 (1)	C(4)-P(2)-C(6)	100.1 (4)
Ni(a)-Ni-P(2a)	126.3	H(1)-P(1)-C(1)	90.2 (2.8)	P(1)-C(1)-C(2)	108.7 (5)
Ni-P(1)-C(1)	129.3 (2)	P(1)-Ni-Ni(a)	53.9	C(2)-C(1)-C(3)	109.4 (6)
C(1)-P(1)-Ni(a)	129.3 (2)	P(1)-Ni-Ni(a)	107.8 (1)	C(2)-C(1)-C(3a)	109.4 (6)
Ni-P(2)-C(5)	115.2 (3)	Ni(a)-Ni-P(1a)	53.9	Ni-Ni(a)-P(1a)	53.9
Ni-P(2)-C(6)	99.4 (3)	P(2)-Ni-P(2a)	107.4 (1)	P(1)-Ni(a)-P(1a)	107.8 (1)
C(5)-P(2)-C(6)	99.4 (3)	P(1a)-Ni-P(2a)	118.4 (1)	H(1)-P(1)-Ni	120.0 (2.1)
P(1)-C(1)-C(3)	109.4 (5)				

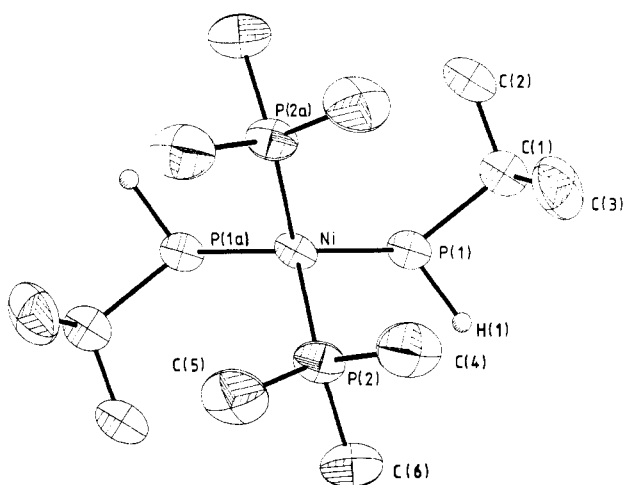


Figure 4. A view of 2 down the Ni-Ni vector. The PMe_3 groups on Ni(a) are omitted for clarity.

strain. The P(1)-P(1a) separation is 3.08 Å which rules out a significant interaction between the two bridging phosphorus atoms.

Experimental Section

All operations were performed under nitrogen. Microanalytical data were by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Proton and phosphorus nuclear magnetic resonance spectra were obtained at 90.0 and 32.299 MHz, respectively, on Varian EM-390 (1H) and FT-80 (^{31}P) spectrometers. Proton chemical shifts are reported in δ units (parts per million relative to Me_4Si , δ 0.0), and phosphorus chemical shifts are in parts per million relative to 85% H_3PO_4 ; positive values are to high frequency in both cases. Spectra were obtained in benzene- d_6 solution at ambient temperature unless otherwise stated. IR spectra were obtained on a Perkin-Elmer 1330 spectrophotometer. Nujol mulls were run by using KBr plates. Melting points were in sealed capillaries under nitrogen (1 atm) and are uncorrected.

[Rh(μ - $(t\text{-Bu})(H)P)(PMe_3)_2$] $_2$ (1). A suspension of $[Rh(CO_2D)Cl]_2$ (0.95 g, 1.93 mmol) in hexane (100 mL) was cooled to $-100^\circ C$, and a solution of $Li_2P\text{-}t\text{-Bu}$ in THF (2.4 mL of a 0.811 M solution, 1.93 mmol) was added dropwise. The mixture was stirred (10 h) and allowed to warm to room temperature. The intense red-purple solution was recooled to $-100^\circ C$, and excess PMe_3 (2.0 mL, 10.0 mmol) was added. The mixture was again allowed to warm to room temperature (2 h). Volatile materials were removed under vacuum, and the residue was extracted with hexane (40 mL). The solution was filtered, evaporated to ca. 10 mL, and

cooled to $-40^\circ C$. After 16 h a large crystalline mass of 1 had formed. This was isolated and dried under vacuum: yield 1.13 g (85%); mp $219\text{-}221^\circ C$ dec; IR (Nujol mull) 2140 (m), 1410 (m), 1340 (w), 1280 (w), 1260 (m), 1010 (w), 915 (s), 825 (w), 790 (w), 640 (m) cm^{-1} ; 1H NMR δ 0.80 (br m, overlapping $(t\text{-Bu})HP$ and PMe_3 resonances) (the $(t\text{-Bu})HP$ resonance was not observed); $^{31}P\{^1H\}$ NMR, see text; the best simulation of the $A_2A_2'M_2X_2$ spin system was obtained by using the following values, δ 207.25 (triplet of pentuplets, μ - $(t\text{-Bu})HP$); $^1J_{Rh-P} = 150.9$ Hz, $^2J_{PMe_3-P-t\text{-Bu}H} = 17.23$ Hz, -10.5 (doublet of triplets plus additional lines between, PMe_3); $^1J_{Rh-P} = 156.8$ Hz, $^2J_{PMe_3-P-t\text{-Bu}H} = 17.2$ Hz, $^2J_{PMe_3-PMe_3} = 10$ Hz, $^1J_{Rh-Rh} = 200$ Hz). Anal. Calcd for $C_{20}H_{56}P_6Rh_2$: C, 34.87; H, 8.10; P, 27.02. Found: C, 35.49; H, 8.38; P, 26.38.

[Ni(μ - $(t\text{-Bu})(H)P)(PMe_3)_2$] $_2$ (2). $NiCl_2(PMe_3)_2$ (2.11 g, 7.4 mmol) was suspended in hexane (80 mL) at $-100^\circ C$, and $Li_2P\text{-}t\text{-Bu}$ (7.38 mmol) in 9.1 mL of an 0.811 M THF solution was added via syringe. The reaction mixture was stirred for 12 h during which time the deep red-brown solution was allowed to warm to room temperature. Volatile materials were removed under vacuum, and the residue was extracted with hexane (40 mL). The solution was filtered, concentrated to 15 mL, and cooled to $-40^\circ C$. After 48 h a substantial amount of black solid was formed that was separated from the solution. The solid was redissolved in hexane (40 mL) to give an intense purple solution. This was filtered, concentrated (15 mL), and cooled ($-40^\circ C$). After 48 h large, deep purple crystals had formed and they were isolated and dried under vacuum: yield 1.85 g, 85%; mp the compound decomposed slowly over the range $195\text{-}235^\circ C$; IR (Nujol mull) 2160 (m), 1420 (m), 1340 (w), 1280 (w), 1250 (m), 1165 (w), 1080 (br s), 1015 (br s), 925 (s), 900 (w), 810 (s), 790 (s), 640 (m) cm^{-1} ; 1H NMR δ 0.75 (br m, overlapping $t\text{-Bu}P$ and PMe_3), 5.07 (d, $^1J_{P-H} = 135.5$ Hz, $HP\text{-}t\text{-Bu}$); $^{31}P\{^1H\}$ δ 160.00 (s), 136.54 (s, $t\text{-Bu}PH$), -22.13 (s), -32.00 (s, PMe_3) (see text). Anal. Calcd for $C_{20}H_{56}Ni_2P_6$: C, 40.00; H, 9.33; P, 31.00. Found: C, 39.37; H, 8.54; P, 30.38.

X-ray Analysis of 1. Crystals of 1 were grown from hexane solution at $-20^\circ C$. They were sealed under nitrogen in Lindemann capillaries and mounted on an Enraf-Nonius CAD-4 diffractometer. With use of the program SEARCH, a program on the CAD-4 that automatically searches for the centers on strong reflections, the initial lattice parameters were determined with $10^\circ < 2\theta < 20^\circ$ and subsequently refined by using higher angle data ($35^\circ < 2\theta < 40^\circ$). Data were collected by using graphite-monochromated radiation. The diffracted intensities were collected by using the ω - 2θ scan method with $1.0^\circ < 2\theta < 40.0^\circ$. The scan rate was varied according to a prescan at $20^\circ \text{ min}^{-1}$, and calculated speeds based on the net intensity gathered ranged from 20 to $0.8^\circ \text{ min}^{-1}$. Moving crystal-moving counter backgrounds were collected for 25% of the total scan width at each end of the scan range. In each intensity the scan width was determined by the equation: scan range = $A + B \tan \theta$ with $A = 0.8^\circ$ and $B = 0.2^\circ$. Aperture settings were determined in a like manner with $A = 4.0$ mm and $B = 1.0$ mm. As a check on the stability of the crystal, three reflections were measured every hour and showed

an overall drop in intensity of <4%. One independent quadrant of data was collected, giving a total of 1729 unique measured reflections for which 792 were considered observed with $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and decay effects but not for absorption ($\mu = 11.60 \text{ cm}^{-1}$).

For both 1 and 2 the cell dimensions and systematic absences indicated a C-centered monoclinic lattice. Of the three possible space groups, $C2/m$ was chosen on the basis of successful refinement in both cases.

The structure was solved by using MULTAN²⁴ which revealed the positions of the rhodium and phosphorus atoms. Subsequent difference Fourier maps revealed the positions of all other non-hydrogen atoms. The structure was refined (full-matrix least squares) with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom H(1) was located and refined positionally, but all others were constrained to idealized geometries 0.96 Å from the respective carbon atom with fixed isotropic thermal parameters. In the final least-squares cycles, refinement converged smoothly to give final residuals $R = 0.044$ and $R_w = 0.049$. No chemically significant peaks were observed in the final difference map. All calculations were performed by using the SHELX²⁵ program package on a UNIVAC 1100/60 computer system. Atomic thermal parameters, details of hydrogen atomic coordinates, and tables of observed and calculated structure factors are available.²³

X-ray Analysis of 2. Crystals of 2 were grown from hexane solutions at -20 °C and sealed in Lindemann capillaries under nitrogen. Final lattice parameters were determined from a least-squares refinement of the angular settings of 25 reflections $25^\circ < 2\theta < 35^\circ$ accurately centered on a Nicolet R3m/E diffractometer. Data were collected by using graphite-monochromated radiation. The diffracted intensities were collected by using the $\theta/2\theta$ scan method with $3.0^\circ < 2\theta < 45^\circ$. The scan rate was variable and was determined from a 2-s prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 3.91 to 29.30° min⁻¹. As a check on crystal stability two check reflections were measured every 50 reflections and showed no appreciable drop in intensity during data collection.

One independent quadrant of data was collected, giving a total of 1158 independent reflections for which 1059 were considered observed with $I > 3\sigma(I)$. These intensities were corrected for Lorentz, polarization, and absorption effects. Absorption was corrected for using the empirical psi scan method with transmission coefficients ranging from 0.369 to 0.537.

The structure was solved by conventional heavy-atom techniques (Patterson and difference Fourier). The nickel atom was located from the Patterson map and all other non-hydrogen atoms from subsequent difference Fourier maps.

The structure was refined (full-matrix blocks, blocked cascade method) with anisotropic thermal parameters for all non-hydrogen atoms. Complex neutral atom scattering factors were employed throughout.²⁶ The hydrogen atom H(1) was located and refined positionally, but all others were constrained to idealized geometries 0.96 Å from the respective carbon atom with fixed isotropic thermal parameters. In the final cycles of refinement a weighting scheme $w = (\sigma^2(F_o) + 0.0036F_o^2)^{-1}$, was introduced and refinement converged smoothly to give final residuals $R = 0.0605$ and $R_w = 0.0655$. No chemically significant peaks were present in the final difference map. All calculations were performed on an Eclipse S140 computer using the SHELX²⁷ program package of the Nicolet R3m system. Atomic thermal parameters, details of hydrogen atomic coordinates, and tables of observed and calculated structure factors are available.²³

Resonance Raman. Resonance Raman spectra were obtained by using a SPEX 1403 spectrometer equipped with a thermoelectrically cooled RCA C31034A photomultiplier tube, a Princeton Applied Research Model 1112 photon counting system, and a Nicolet 1180E Raman data system. Spectra were typically obtained with a spectral slit width of 5 cm⁻¹ and a digital resolution of 0.4 cm⁻¹. The spectral scan rate was 1 cm⁻¹ s⁻¹ with no analogue time constant employed. Typical signal averaging utilized 5–10 coadded scans. Thus the durability of the sample could be assessed during acquisition of a spectrum by observing the quality of any given scan. Laser excitation was provided by a Spectra-Physics 171-01 Ar⁺ laser (514.5 nm). Laser power was typically 10 mW at the sample. A spinning cell arrangement was used to contain the sample tube.²⁷ The backscattered radiation was collected at 135° normal to the incident laser radiation.

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Registry No. 1, 87040-41-3; 2, 87040-42-4.

Supplementary Material Available: Tables of atomic thermal parameters for 1 and 2, hydrogen atomic coordinates for 2, and structure factors (14 pages). Ordering information is given on any current masthead page.

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