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Synthesis and Structure of Hydrido Bis(ethylene) and Hydrido Dinitrogen Complexes of Rhenium(I) Having Dimethylphenylphosphine Ligands

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mer-Hydridobis(ethylene)tris(dimethylphenylphosphine)rhenium(I) (1) and *cis*-hydrido(dinitrogen)tetrakis(dimethylphenylphosphine)rhenium(I) (2) have been prepared by the reaction of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(I) with ethyllithium and *n*-propyllithium, respectively. X-ray structure analysis reveals that both complexes are octahedral, and in the former complex the two coordinated ethylenes occupy sites perpendicular to each other in cis positions and in the latter complex hydrido and dinitrogen ligands in cis positions. The coordinated ethylene and dinitrogen can be smoothly displaed by dihydrogen to give known trihydrido- or pentahydridorhenium complexes. Crystal data for 1: space group $P\bar{1}$, $Z = 2$, $a = 9.285$ (3) Å, $b = 19.229$ (5) Å, $c = 9.044$ (3) Å, $\alpha = 93.47$ (3)°, $\beta = 120.16$ (2)°, $\gamma = 90.23$ (3)°, $V = 1392.5$ (8) Å^3, $R = 0.0653$, $R_w = 0.0641$, based on 3959 reflections with $F > 3\sigma(F)$. Crystal data for 2: space group $P2_1/a$, $Z = 4$, $a = 27.49$ (1) Å, $b = 10.113$ (2) Å, $c = 12.235$ (6) Å, $\beta = 91.94$ (4)°, $V = 3424$ (2) Å^3, $R = 0.0464$, $R_w = 0.0533$, based on 4129 reflections with $F > 3\sigma(F)$.

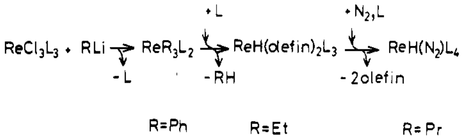
Introduction

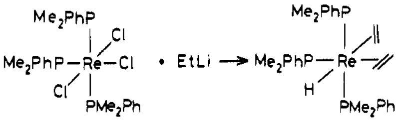
Of all transition metals, rhenium has one of the more diverse families of hydrides.[1] These complexes are a convienient entry to intriguing organorhenium chemistry, since they liberate hydrogen to offer reactive, coordinatively unsaturated complexes. In fact, some of them are capable of activating stable C-H bonds.[2] Hydrido complexes containing weakly coordinated ligands such as olefins and dinitrogen are also of interest in a similar vein. However, rhenium(I) dinitrogen complexes are among the most stable dinitrogen complexes of transition metals known.[3] Thus, the coordinated dinitrogen has usually less tendency to be replaced by other ligands, although photochemical reactions dissociate dinitrogen in some cases.[4] On the other hand, olefin complexes of rhenium(I) are rather rare. One unusual preparative example is the platinum-catalyzed formation of a hydridobis(ethylene)bis(diisopropylphenylphosphine)rhenium(I) from the rhenium heptahydrido complex.[5] Another example is the hydridoethylenerhenium(I) complex, which can be prepared by the ligand-exchange reaction of $ReH(N_2)(dpe)_2$ with pressurized ethylene. We report here the preparation and structure of novel hydrido ethylene and hydrido dinitrogen complexes of rhenium(I) having dimethylphenylphosphine ligands.

Results and Discussion

Preparation of *mer*-Hydridobis(ethylene)tris(dimethyphenylphosphine)rhenium(I) (1). Treatment of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III)[6] with ethyllithium (8 mol/Re) in dry ether at room temperature gave yellow crystals of *mer*-hydridobis(ethylene)tris(dimethylphenylphosphine)rhenium(I) (1) in 54% yield (eq 1). 1 is moderately stable thermally but slowly decomposes under air.

Scheme I. Reaction Pathway of the Formation of 1 and 2





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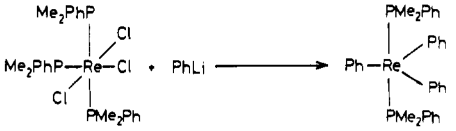
(1)

Complex 1 has been unequivocally characterized by elemental analysis, IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and X-ray structure analysis as well as by chemical reactions. A plausible reaction pathway for the formation of 1 is the initial alkylation followed by β-hydrogen elimination from an ethylrhenium(III) intermediate as shown in Scheme I. The formation of such a trialkylrhenium(III) intermediate is not unreasonable, since alkylation of trichlorotris(dimethylphenylphosphine)rhenium(III) with phenyllithium gave triphenylbis(dimethylphenylphosphine)rhenium(III) (eq 2). A similar triphenylrhenium(III) derivative having diethylphenylphosphine ligands is also known.[7]



(2)

The presence of a hydrido ligand in 1 is confirmed by ^{1}H NMR, which shows well-resolved double triplets at δ -4.7 as well as by the IR showing a ν(Re-H) band at 1915 cm^{-1}. Methyl signals of PMe_2Ph ligands are observed as a doublet and two triplets at δ 1.0, 1.2, and 1.3, respectively.

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[1] (a) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleaverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 4, p 125 and references cited therein. (b) Boag, N. M.; Kaesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, J., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol 4, p 161.

[2] For example: (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1244; **1982**, 606. (b) Jones, W. D.; Fan, M. *Organometallics* **1986**, *5*, 1057. (c) Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Zhang, J.-M.; Sutton, D. *J. Am. Chem. Soc.* **1989**, *111*, 3468. (d) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

[3] Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612.

[4] (a) Oliva, A. H. K.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107. (b) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (c) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1983**, *248*, C26.

[5] Hazel, N. J.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1663.

[6] Parshall, G. W. *Inorg. Synth.* **1977**, *17*, 110.

[7] Chatt, J.; Garforth, J. D.; Rowe, G. A. *J. Chem. Soc. A* **1966**, 1834.

0276-7333/91/2310-3105$02.50/0

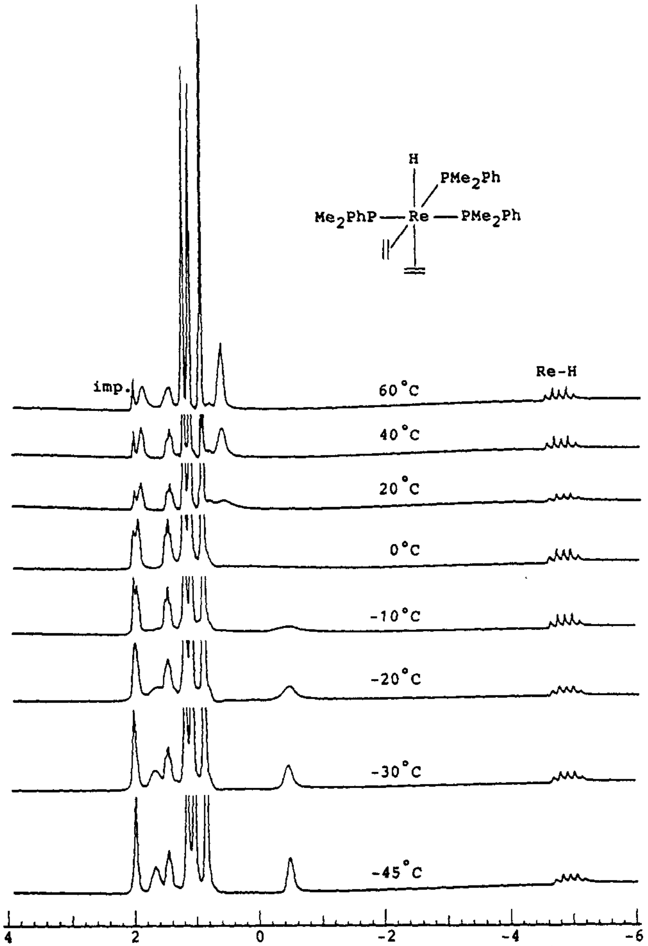


Figure 1. Variable-temperature ^1H NMR spectrum of $ReH(C_2H_4)_2(PMe_2Ph)_3$ in toluene-d_8 at 200 MHz.

A broad signal at δ 0.9 (4 H) and a pair of signals at δ 1.6 and 2.1 (2 H each) may be assigned to the two coordinated ethylene protons. The $^{31}P\{^1H\}$ NMR of 1 shows a doublet and a triplet at −15.0 and −30.7 ppm from external PPh_3 in a 2:1 ratio. These spectroscopic results are consistent with the proposed meridional structure of 1, in which two PMe_2Ph ligands trans to each other and one unique PMe_2Ph ligand are included. The two ethylene ligands are magnetically inequivalent and occupy sites trans to the unique P ligand and hydride, respectively. Figure 1 demonstrates the temperature dependence of ^1H NMR showing dynamic behavior of these protons. Thus, when the toluene-d_8 solution of 1 is cooled to −62 °C, the broad signal of coordinated ethylenes at 0.9 ppm gradually broadened further and finally separated into two broad signals at δ −0.35 and 1.82 in a 1:1 ratio. The coalescence temperature is 0 °C. Other signals in ^1H NMR as well as those in ^{31}P NMR are relatively insensitive to temperature. These results suggest that one of the coordinated ethylene ligands, presumably the ethylene trans to hydride, which generally slows high trans influence, rotates by the NMR time scale at ambient temperature without significant structural rearrangement. The estimated $\Delta G^\ddagger$ value for the rotation was 12.2 kcal/mol (0 °C).

Thermolysis and Acidolysis. Thermolysis of 1 at 60 °C in Ph_2O smoothly liberated ethylene (117%/Re) and ethane (65%), the total amount supporting the chemical formula of 1. Formation of a significant amount of ethane indicates that the hydrogenation of ethylene took place at least in part, although the hydrogen source is not clear. Unfortunately, catalytic hydrogenation of ethylene was unsuccessful even under atmospheric hydrogen at room temperature. Acidolysis of 1 with concentrated sulfuric acid also gave ethylene (78%) and ethane (100%).

Table I. Summary of Crystallographic Data for 1 and 2

	1	2
formula	$C_{28}H_{42}P_3Re$	$C_{32}H_{45}N_2P_4Re$
fw	657.8	768.8
space group	$P\bar{1}$	$P2_1/a$
crystal system	triclinic	monoclinic
a, Å	9.285 (3)	27.49 (1)
b, Å	19.229 (5)	10.113 (2)
c, Å	9.044 (3)	12.325 (6)
α, deg	93.47 (3)	
β, deg	120.16 (2)	91.94 (4)
γ, deg	90.23 (3)	
V, Å^3	1392.5 (8)	3424 (2)
Z	2	4
d_{calcd}, g cm^{-3}	1.569	1.330
radiation (λ, Å)	Mo Kα (0.71068)	Mo Kα (0.71068)
μ(Mo Kα), cm^{-1}	43.4	35.8
temp, °C	−20	room temp
2θ, deg	$3 < 2\theta < 50$	$3 < 2\theta < 50$
scan type	ω/2θ	ω/2θ
no. of data collected	4899	5804
no. of obsd reflcns for refinement	3959 ($F_o > 3\sigma(F_o)$)	4129 ($F_o > 3\sigma(F_o)$)
R^a	0.0653	0.0464
R_w^b	0.0641	0.0533
method of phase determin	heavy-atom	heavy-atom

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum(w[|F_o| - |F_c|]^2)/\sum w(|F_o|)^2]^{1/2}$.

Table II. Fractional Atomic Coordinates (×10^4) for 1

atom	x	y	z	B_{eq}, Å^2
Re	5971.1 (6)	7833.8 (2)	5788.5 (6)	2.64 (1)
P(1)	3525 (4)	7574 (2)	3004 (4)	3.2 (1)
P(2)	5531 (4)	6795 (2)	6842 (4)	3.4 (1)
P(3)	7209 (4)	8627 (2)	4756 (5)	3.5 (1)
C(1)	8590 (17)	7692 (7)	7757 (16)	3.8 (5)
C(2)	7852 (19)	8207 (7)	8383 (19)	4.2 (5)
C(3)	4300 (19)	8239 (7)	6765 (20)	4.3 (6)
C(4)	4694 (19)	8781 (7)	5982 (20)	4.3 (6)
C(5)	8057 (22)	8242 (9)	3502 (22)	4.8 (7)
C(6)	6033 (20)	9329 (8)	3362 (22)	4.8 (6)
C(7)	9012 (16)	9187 (6)	6363 (17)	3.9 (5)
C(8)	10669 (17)	9006 (8)	6918 (19)	4.5 (5)
C(9)	11980 (19)	9434 (9)	8137 (23)	5.5 (6)
C(10)	11716 (21)	10029 (9)	8830 (22)	5.5 (7)
C(11)	10094 (23)	10228 (8)	8281 (21)	5.7 (7)
C(12)	8754 (19)	9799 (7)	7053 (18)	4.4 (5)
C(13)	1482 (17)	7694 (9)	2808 (25)	5.3 (7)
C(14)	3146 (21)	8052 (8)	1134 (20)	4.5 (6)
C(15)	3235 (16)	6681 (7)	1954 (16)	3.5 (5)
C(16)	4566 (17)	6351 (7)	2064 (19)	4.4 (5)
C(17)	4345 (23)	5686 (9)	1178 (23)	6.3 (7)
C(18)	2767 (23)	5376 (8)	212 (21)	5.9 (7)
C(19)	1424 (22)	5716 (8)	69 (22)	5.8 (7)
C(20)	1615 (20)	6373 (7)	922 (20)	5.2 (6)
C(21)	6492 (20)	6022 (7)	6505 (22)	5.0 (6)
C(22)	6347 (23)	6791 (9)	9146 (20)	5.6 (7)
C(23)	3411 (16)	6448 (7)	6130 (16)	3.9 (5)
C(24)	2669 (19)	5902 (7)	4836 (19)	4.7 (6)
C(25)	1051 (24)	5668 (10)	4229 (24)	6.8 (8)
C(26)	84 (24)	5990 (11)	4861 (27)	7.8 (9)
C(27)	806 (22)	6528 (9)	6117 (27)	7.2 (8)
C(28)	2445 (20)	6751 (8)	6768 (21)	5.4 (6)

Description of the Molecular Structure of 1. Crystallographic data for 1 are summarized in Table I. Fractional atomic coordinates and selected bond angles and distances are listed in Tables II and III. As shown in Figure 2, the molecular structure of 1 is essentially octahedral and the three phosphorus ligands occupy meridional positions as expected from NMR analysis. The hydrido ligand presumably occupies the site trans to one

Table III. Selected Bond Lengths and Angles for 1

(a) Bond Lengths, Å

Re-P(1)	2.418 (3)	P(1)-C(13)	1.83 (2)
Re-P(2)	2.383 (4)	P(1)-C(14)	1.85 (2)
Re-P(3)	2.400 (4)	P(1)-C(15)	1.86 (1)
Re-C(1)	2.21 (1)	P(2)-C(21)	1.82 (2)
Re-C(2)	2.18 (1)	P(2)-C(22)	1.83 (2)
Re-C(3)	2.26 (2)	P(2)-C(23)	1.84 (2)
Re-C(4)	2.22 (2)	P(3)-C(5)	1.81 (2)
C(1)-C(2)	1.45 (3)	P(3)-C(6)	1.85 (2)
C(3)-C(4)	1.44 (3)	P(3)-C(7)	1.85 (1)

(b) Bond Angles, deg

P(1)-Re-P(2)	92.0 (1)	C(21)-P(2)-C(23)	101.3 (7)
P(1)-Re-P(3)	94.1 (1)	C(22)-P(2)-C(23)	97.5 (9)
P(2)-Re-P(3)	160.0 (1)	C(5)-P(3)-Re	116.3 (6)
C(1)-Re-C(2)	38.6 (6)	C(6)-P(3)-Re	122.5 (7)
C(3)-Re-C(4)	37.4 (7)	C(7)-P(3)-Re	117.7 (6)
C(13)-P(1)-Re	117.8 (7)	C(5)-P(3)-C(6)	99.1 (9)
C(14)-P(1)-Re	121.2 (5)	C(5)-P(3)-C(7)	100.5 (8)
C(15)-P(1)-Re	118.3 (4)	C(7)-P(3)-C(6)	96.6 (6)
C(13)-P(1)-C(14)	97.1 (9)	C(8)-C(7)-P(3)	122 (1)
C(13)-P(1)-C(15)	101.3 (7)	C(12)-C(7)-P(3)	120 (1)
C(15)-P(1)-C(14)	96.7 (7)	C(16)-C(15)-P(1)	119.7 (9)
C(21)-P(2)-Re	115.6 (7)	C(20)-C(15)-P(1)	120 (1)
C(22)-P(2)-Re	117.6 (6)	C(27)-C(23)-P(2)	150.3 (8)
C(23)-P(2)-Re	121.2 (4)	C(28)-C(23)-P(2)	121 (1)
C(21)-P(2)-C(22)	99.9 (8)		

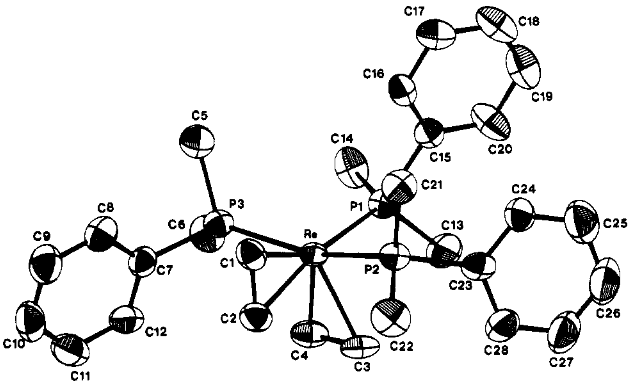
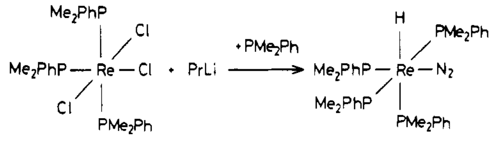


Figure 2. ORTEP drawing of $ReH(C_2H_4)_2(PMe_2Ph)_3$ showing the atomic numbering scheme used. Ellipsoids are drawn at the 50% probability level.

of the ethylene ligands, although it could not be found in the differential map. The Re-P bond distance trans to ethylene (2.418 (3) Å) is slightly longer than those trans to each other (2.383 (4) and 2.400 (4) Å), indicating stronger trans influence of ethylene than dimethylphenylphosphine. An interesting structural feature in 1 is that two ethylene ligands lie perpendicular to each other in cis positions, probably due to the steric repulsion among the ligands. The result is in sharp contrast to the structure of trihydridobis(ethylene)bis(diisopropylphenylphosphine)rhenium(III) in which two ethylene ligands coordinate in a parallel fashion.[5] C=C bond distances of coordinated ethylenes are found to be 1.43 (2) Å, suggesting a small contribution of back-bonding from rhenium. However, observed C-H coupling constants of coordinated ethylene carbons estimated by INEPT (152 and 153 Hz) suggest their essential sp^2 character.

***cis*-Hydrido(dinitrogen)tetrakis(dimethylphenylphosphine)rhenium(I).** An analogous reaction of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(I) with propyllithium under nitrogen gave *cis*-hydrido(dinitrogen)tetrakis(dimethylphenylphosphine)rhenium(I) (2) (eq 3). Atmospheric nitrogen seems to be trapped by the coordinatively unsaturated hydridobis(propylene)rhenium(I) intermediate, which may be formed by β-hydrogen elimination of propylrhenium species as discussed in the formation pathway of 1. Such displacement of the propylene ligand with atmospheric nitrogen may be due to the weaker coordination ability of propylene to rhenium than that of N_2. Although the principal synthetic routes to dinitrogen complexes of rhenium have been indirect rather than from dinitrogen itself,[1] our reaction may rank as a convenient entry for the rhenium dinitrogen complex.



2

(3)

The ^1H NMR spectrum of 2 shows two doublets at δ 1.3 and 1.7 and a triplet at δ 1.5 in a 1:1:2 ratio, which are assignable to methyl protons of dimethylphenylphosphine ligands. The result suggests that two of the dimethylphenylphosphine ligands are magnetically inequivalent, one being trans to hydride and the other trans to dinitrogen, and two other magnetically equivalent phosphorus ligands occupy sites trans to each other. The hydrido proton appears as triplets of a triplet at δ -6.0. The splitting pattern can be accounted for by assuming the accidental coincidence of the coupling constants between the hydrido proton and P nuclei trans to hydride and to dinitrogen ligands, respectively. These results are consistent with the cis configuration for 2. $^{31}P\{^1H\}$ NMR of 2 further supports the proposed structure. Thus, three types of signals are observed at -14.4 (triplet of a triplet), -19.0 (double doublets), and -29.6 ppm (double triplets) in 1:2:1 ratio, consistent with the proposed arrangement of phosphorus ligands.

The IR spectrum of 2 shows stretching bands due to Re-H and N_2 at 1835 and 2000 cm^{-1}. The latter band shifted to 1930 cm^{-1} after treatment of 2 with atmospheric $^{15}N_2$ gas in toluene at room temperature, indicating that the band at 2000 cm^{-1} is $\nu(N_2)$. The result also shows that the coordinated dinitrogen is exchangeable with atmospheric nitrogen, probably via a dissociative route. The $\nu(N_2)$ value observed for 2 is considerably larger than those for other corresponding dinitrogen complexes of rhenium(I) such as *trans*-$ReCl(N_2)(PMe_2Ph)_4$ (1925 cm^{-1})[3] and *trans*-$ReH(N_2)(PEt_2Ph)_4$ (1945 cm^{-1}).[8] The N≡N bond in 2 is much less reduced than expected, since 2 has electron-donating dimethylphenylphosphine and hydrido ligands. This may give rise to the weaker trans influence of a dimethylphenylphosphine ligand than that of chloride and hydride ligands. Competitive back-bonding of the dinitrogen and its trans phosphorus ligands may reduce the trans influence.

Description of the Molecular Structure of 2. Table I summarizes the crystallographic data for 2. Fractional atomic coorindates and selected bond distances and angles are listed in Tables IV and V. An ORTEP drawing of the molecular structure is shown in Figure 3. The structure of 2 is also definitely octahedral, although the hydrido ligand is not found in the differential map. The hydrido ligand is considered to stay on the site trans to one of the phosphorus ligand, since the structure clearly has enough space for one extra ligand there. The N-N bond distance is 1.12 (2) Å. Bond angles between P-Re-P and P-Re-N lie between 86 and 103°, also suggesting slight distortion from the octahedron probably due to the steric repulsion of bulky P ligands.

It should be noted that the dinitrogen and hydrido ligands are cis to each other, although the structures of all analogous dinitrogen complexes of rhenium(I) ever re-

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for 2

atom	x	y	z	B_{eq}, Å^2
Re	6301.0 (2)	3896.9 (5)	1873.9 (3)	3.01 (1)
P(1)	5911 (1)	3337 (3)	3500 (3)	3.62 (8)
P(2)	5868 (1)	2222 (3)	911 (3)	4.1 (1)
P(3)	6505 (1)	6028 (4)	2576 (3)	3.78 (8)
P(4)	7041 (1)	2711 (4)	2124 (3)	4.8 (1)
N(1)	6557 (4)	4476 (12)	492 (9)	4.8 (3)
N(2)	6700 (5)	4825 (15)	−301 (10)	7.0 (5)
C(1)	5271 (5)	3930 (20)	3564 (12)	4.7 (5)
C(2)	5830 (7)	1589 (16)	3867 (13)	5.5 (5)
C(3)	6174 (4)	3845 (13)	4856 (9)	3.6 (3)
C(4)	6656 (6)	3693 (18)	5060 (12)	6.5 (5)
C(5)	6855 (7)	3931 (22)	6066 (15)	7.9 (7)
C(6)	6596 (8)	4444 (23)	6871 (14)	7.6 (7)
C(7)	6112 (10)	4636 (25)	6651 (14)	9.1 (8)
C(8)	5897 (6)	4313 (20)	5684 (13)	6.7 (6)
C(9)	5891 (8)	2390 (19)	−557 (13)	6.2 (6)
C(10)	6018 (7)	469 (16)	1020 (17)	6.7 (6)
C(11)	5199 (4)	2200 (12)	1059 (10)	3.7 (3)
C(12)	4931 (5)	3259 (14)	685 (12)	4.8 (4)
C(13)	4436 (6)	3302 (19)	826 (15)	6.0 (5)
C(14)	4211 (7)	2308 (22)	1340 (16)	6.7 (6)
C(15)	4465 (7)	1240 (20)	1726 (15)	6.9 (6)
C(16)	4967 (6)	1161 (15)	1567 (12)	5.2 (4)
C(17)	6687 (6)	7237 (15)	1525 (14)	6.2 (5)
C(18)	6984 (6)	6390 (16)	3580 (16)	6.3 (6)
C(19)	5991 (5)	6931 (12)	3149 (10)	4.0 (4)
C(20)	5981 (6)	7345 (15)	4201 (12)	5.5 (5)
C(21)	5599 (7)	8005 (18)	4611 (15)	6.3 (6)
C(22)	5177 (8)	8293 (18)	3923 (21)	7.9 (7)
C(23)	5208 (6)	7907 (15)	2887 (16)	5.5 (5)
C(24)	5587 (7)	7228 (13)	2467 (13)	5.4 (5)
C(25)	7117 (8)	1231 (18)	2980 (20)	8.1 (7)
C(26)	7289 (8)	2097 (28)	843 (15)	8.1 (9)
C(27)	7590 (4)	3656 (14)	2558 (12)	4.8 (4)
C(28)	7828 (7)	3527 (18)	3606 (14)	6.1 (5)
C(29)	8195 (7)	4391 (22)	3901 (18)	7.5 (7)
C(30)	8356 (8)	5334 (25)	3207 (23)	9.0 (9)
C(31)	8137 (7)	5441 (25)	2188 (19)	8.3 (8)
C(32)	7755 (7)	4667 (22)	1881 (14)	7.1 (6)

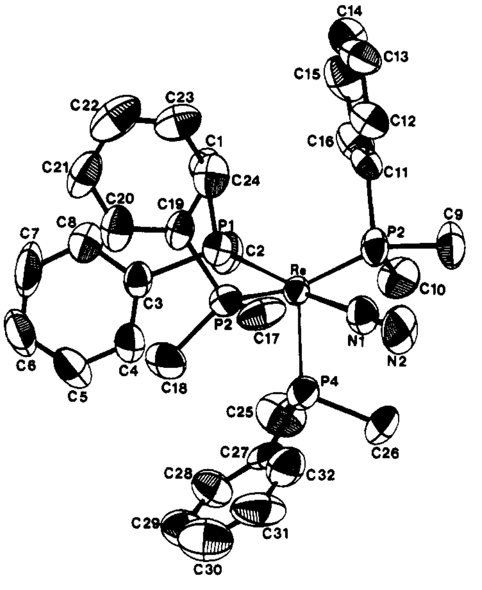


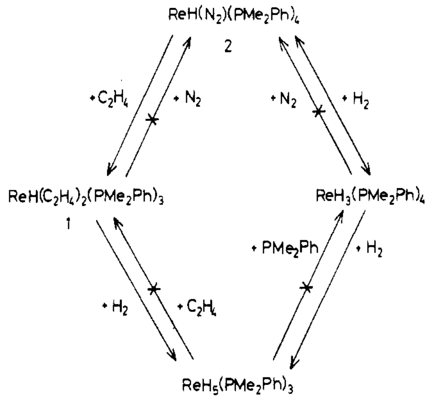
Figure 3. ORTEP drawing of $ReH(N_2)(PMe_2Ph)_4$ showing the atomic numbering scheme used. Ellipsoids are drawn at the 50% probability level.

ported have trans configuration. For example, hydrido(dinitrogen)tetrakis(diethylphenylphosphine)rhenim(I)[8] and hydrido(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]rhenim(I),[9] though they have different types of phosphorus ligands, have been structurally confirmed as trans. The structure of chloro(dinitrogen)tetrakis(dimethylphenylphosphine)rhenim(I), having the same phosphorus ligand as in 2, is also trans. A possible reason for the cis configuration of 2 is the release of steric hindrance among ligands when smaller dimethylphenylphosphine ligands (cone angles are 122° for PMe_2Ph and 136° for PEt_2Ph) are employed as stabilizing ligands. If this is the case, it is concluded that the phosphorus ligands essentially disfavor staying trans to each other.[10]

Table V. Selected Bond Lengths and Angles for 2

(a) Bond Lengths, Å			
Re–P(1)	2.372 (3)	P(2)–C(10)	1.82 (2)
Re–P(2)	2.367 (3)	P(2)–C(11)	1.85 (1)
Re–P(3)	2.382 (4)	P(3)–C(17)	1.86 (2)
Re–P(4)	2.371 (4)	P(3)–C(18)	1.81 (2)
Re–N(1)	1.96 (1)	P(3)–C(19)	1.84 (1)
P(1)–C(1)	1.86 (2)	P(4)–C(25)	1.84 (2)
P(1)–C(2)	1.84 (2)	P(4)–C(26)	1.85 (2)
P(1)–C(3)	1.87 (1)	P(4)–C(27)	1.85 (1)
P(2)–C(9)	1.82 (2)	N(1)–N(2)	1.12 (2)
(b) Bond Angles, deg			
N(1)–Re–P(1)	173.6 (4)	Re–P(2)–C(10)	123.4 (7)
N(1)–Re–P(3)	87.6 (4)	Re–P(2)–C(11)	116.3 (4)
N(1)–Re–P(4)	86.1 (4)	C(9)–P(2)–C(10)	98.6 (9)
P(1)–Re–P(2)	91.1 (1)	C(9)–P(2)–C(11)	99.6 (8)
P(1)–Re–P(3)	91.0 (1)	C(10)–P(2)–C(11)	101.8 (8)
P(1)–Re–P(4)	100.3 (1)	Re–P(3)–C(17)	114.0 (5)
P(2)–Re–P(3)	159.7 (1)	Re–P(3)–C(18)	126.0 (6)
P(2)–Re–P(4)	96.7 (1)	Re–P(3)–C(19)	114.5 (4)
P(3)–Re–P(4)	102.7 (1)	C(17)–P(3)–C(18)	97.8 (8)
Re–N(1)–N(2)	180 (1)	C(17)–P(3)–C(19)	99.7 (6)
Re–P(1)–C(1)	114.4 (5)	C(18)–P(3)–C(19)	100.7 (7)
Re–P(1)–C(2)	120.0 (6)	Re–P(4)–C(25)	124.5 (7)
Re–P(1)–C(3)	121.2 (4)	Re–P(4)–C(26)	113.5 (7)
C(1)–P(1)–C(2)	100.1 (9)	Re–P(4)–C(27)	117.7 (5)
C(1)–P(1)–C(3)	102.2 (6)	C(25)–P(4)–C(26)	100 (1)
C(2)–P(1)–C(3)	95.2 (7)	C(25)–P(4)–C(27)	100.3 (8)
Re–P(2)–C(9)	113.4 (6)	C(26)–P(4)–C(27)	96.7 (9)

Scheme II. Ligand-Exchange Reaction of 1 and 2 with Ethylene, Nitrogen, and Hydrogen



Displacement among Coordinated Ethylene, Dinitrogen, and Hydrido Ligands. Complexes 1 and 2 are more susceptible to ligand exchange in comparison with known hydridorhenium(I) complexes. Results are summarized in Scheme II. When 1 atm of hydrogen gas was brought in contact with a toluene solution of 1 at room temperature, pentahydridotris(dimethylphenylphosphine)rhenium(I)[11] smoothly formed accompanied by liberation of ethylene and ethane. Partial hydrogenation

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[8] Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. K.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

[9] Tully, M. E.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1973**, *95*, 2042.

[10] The reason for the cis configuration of 2 is not clear at present, and further structural information concerning related hydrido(dinitrogen)rhenium complexes is desired.

[11] Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64.

of ethylene was observed during the reaction. A reverse reaction of pentahydridorhenium(I) complex with ethylene did not take place. On the other hand, 2 reacted with ethylene to give 1 with liberation of nitrogen and a dimethylphenylphosphine ligand. The reaction again was not reversible. In the presence of 1 atm of hydrogen in benzene, 2 was slowly converted to pentahydridotris(dimethylphenylphosphine)rhenium(I) in 10 h at room temperature. ^{1}H NMR analysis of the reaction mixture after 5 h indicated the existence of both trihydridotetrakis(dimethylphenylphosphine)rhenium(I)[12] and pentahydridotris(dimethylphenylphosphine)rhenium(I) in a ca. 1:1 ratio. The results suggest that the reaction proceeds in a stepwise manner. Thus, the initial displacement of dinitrogen by dihydrogen takes place, followed by further displacement of dimethylphenylphosphine ligand by dihydrogen to give the pentahydridorhenium(I) complex. In these reactions, backward reaction was not successful even under photolysis conditions. From these results, it can be concluded that the coordination ability of these ligands to Re(I) is in the order $N_2 < C_2H_4 < H_2$.

Experimental Section

All manipulations were carried out under deoxygenated nitrogen or argon. Solvents were purified by standard methods under nitrogen and stored under nitrogen before use. Dimethylphenylphosphine was prepared from phenyldichlorophosphine and Grignard reagent. Alkyllithiums were prepared from Li metal and alkyl chloride in pentane. $ReCl_3(PMe_2Ph)_3$ was prepared by a literature method.[6] IR spectra were recorded on Jasco IR A302 and FTIR 5M spectrometers. NMR spectra were measured by using JEOL NMR FX-200 and FX90Q spectrometers. Elemental analyses were performed with a Yanagimoto CHN autocorder MT-2. Gases were quantitatively analyzed either by GC using the internal standard method or by GC after the gasses were collected with a Toepler pump and the gas volume measured.

Crystal Structure Analysis. Most of the apparently appropriate yellow platelike crystals of 1 grown from ether were found to contain cracks, as revealed by oscillation photograph analysis. Therefore a transparent part of the crystal (0.3 × 0.4 × 0.2 mm), which was obtained by careful cutting of the medium-size crystals, was selected. Yellow crystals suitable for X-ray analysis for 2 were obtained from recrystallization from ether, and small crystals (0.2 × 0.2 × 0.2 mm) were selected in order to avoid absorption effect. Both crystals were mounted in a capillary tube under nitrogen. Intensity data for 1 and 2 were collected on a Rigaku AFC-5 diffractometer at -20 °C and at room temperature, respectively. The structure of the compounds was solved by the heavy-atom method and refined by a full-matrix least-squares procedure. In both cases, empirical absorption correction[13] was applied after all the non-hydrogen atoms were located. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, which were either found in the differential map or estimated by theoretical calculation, were included in the calculation, but they were not refined. Data collection and calculations were carried out with the program CRYSTAN (Rigaku).

***mer*-Hydridobis(ethylene)tris(dimethylphenylphosphine)rhenium(I).** An excess of ethyllithium (7.83 mmol) was added to an ethereal solution (10 cm^3) of $ReCl_3(PMe_2Ph)_3$ (628.5 mg, 0.889 mmol). The color of the solution changed from orange to green and finally to orange again in 2 h at room temperature. After careful hydrolysis of the solution, the organic layer was extracted with ether a few times. Recrystallization of the red-brown solid gave light yellow plates. The pure compound can be obtained by repeated recrystallization. Yield: 35%. Mp: 112–114 °C. Anal. Calcd for $C_{28}H_{42}P_3Re$: C, 51.13; H, 6.44. Found: C, 50.76; H, 6.47. IR: ν(Re–H) = 1915 cm^{-1}. Selected ^{1}H NMR (C_6D_6): δ –4.7 (dt, 1 H, ReH, J(PH) = 44.9, 23.4 Hz), 0.8 (br, 4 H, C_2H_4), 1.0 (d, 6 H, PMe, J(PH) = 5.9 Hz), 1.2 (t, 6 H, PMe, J(PH) = 2.9 Hz), 1.3 (t, 6 H, PMe, J(PH) = 2.9 Hz), 1.6, 2.1 (br, 2 H each, C_2H_4). ^{13}C{^{1}H} NMR (C_6D_6): 15.9 (t, PMe, J(CP) = 14.7 Hz), 17.1 (t, PMe, J(CP) = 14.7 Hz), 18.9 (d, PMe, J(CP) = 24.4 Hz), 23.0, 24.4 ppm (br, C_2H_4). ^{31}P{^{1}H} (from external PPh_3): –30.7 (t, J(PP) = 8.5 Hz), –15.0 ppm (d, J(PP) = 8.5 Hz).

***cis*-Hydrido(dinitrogen)tetrakis(dimethylphenylphosphine)rhenium(I).** To an ethereal solution containing $ReCl_3(PMe_2Ph)_3$ (1.04 g, 1.47 mmol) and PMe_2Ph (1.46 mmol) was slowly added *n*-propyllithium (11.7 mmol). The color of the solution changed from orange to green and then to orange. After being stirred for 2 h at room temperature, the solution was slowly hydrolyzed. Recrystallization of ether extracts gave yellow prisms. Yield: 640 mg, 57%. Mp: 127–130 °C. IR: ν(Re–H) = 1835, ν(N═N) = 2000 cm^{-1}. Anal. Calcd for $C_{32}H_{45}N_2P_4Re$: C, 50.06; H, 5.91; N, 3.56. Found: C, 49.42; H, 6.18; N, 3.71. Selected ^{1}H NMR (C_6D_6): δ –6.0 (tt, 1 H, ReH, J(PH) = 18.1, 26.4 Hz), 1.3 (d, 6 H, PMe, J(PH) = 6.4 Hz), 1.5 (t, 12 H, PMe, J(PH) = 2.7 Hz), 1.7 (d, 6 H, PMe, J(PH) = 5.4 Hz). ^{13}C{^{1}H} NMR (C_6D_6): 21.1 (t, PMe trans to each other, J(PC) = 12.8 Hz), 23.1 (t, PMe trans to each other, J(PC) = 13.4 Hz), 23.3 (d, PMe, J(PC) = 22.0 Hz), 26.7 ppm (d, PMe, J(PC) = 27.5 Hz). ^{31}P{^{1}H} NMR (C_6D_6): –14.4 (dt, J(PP) = 12.2, 18.3 Hz), –19.0 (dd, J(PP) = 7.3, 18.3 Hz), –29.6 ppm (dt, J(PP) = 12.2, 7.3 Hz).

2 (50.0 mg 0.0651 mmol) was dissolved in toluene (1.0 cm^3) and the resultant solution degassed. $^{15}N_2$ gas (ca. 10 cm^3) was introduced and the mixture stirred for 1 day. Removal of all the volatile matter gave a yellow solid. The IR spectrum of the yellow solid showed a ν(^{15}N═^{15}N) band at 1930 cm^{-1} and ν(Re—H) remained unchanged.

Triphenylbis(dimethylphenylphosphine)rhenium(III). Phenyllithium (4.69 mmol) was added to an ethereal solution of *mer*-$ReCl_3(PMe_2Ph)_3$ (373.9 mg, 0.529 mmol) to give a blue solution. After 2 h of stirring, the solution was hydrolyzed. Ether extracts were redissolved in benzene and purified by column chromatography using silica gel. Recrystallization from pentane gave blue crystals. Yield: 136.7 mg, 37%. Mp: 95–98 °C. Anal. Calcd for $C_{34}H_{37}P_2Re$: C, 58.86; H, 5.38. Found: C, 58.45; H, 5.74. ^{1}H NMR: δ 1.1 (t, 12 H, J(PH) = 2.4 Hz), 6.2 (d, 6 H, *o*-H of RePh, J(HH) = 7.8 Hz), 6.4 (t, 3 H, *p*-H of RePh, J(HH) = 7.8 Hz), 6.6 (br, 4 H, *o*-H of PhP), 7.0 (br, 6 H, *m*- and *p*-H of PhP), 7.1 (t, 6 H, *m*-H of RePh, J(HH) = 7.8 Hz).

Acidolyses of 1 and 2. 1 (0.0079 mmol) was placed in a Schlenk-type flask with a serum cap and degassed. Sulfuric acid (0.5 cm^3) was added by hypodermic syringe to liberate ethylene (0.0062 mmol, 78%) and ethane (0.0079 mmol, 100%) immediately. Similar reaction of 2 (0.058 mmol) afforded nitrogen (0.0621 mmol, 107%) and hydrogen (0.0592 mmol, 102%).

Thermolysis of 1. A Schlenk-type flask containing 1 (0.0158 mmol) in diphenyl ether (1.0 cm^3) was degassed and the mixture heated to 60 °C for 27 h. Ethylene (0.0185 mmol, 117%) and ethane (0.102 mmol, 65%) were detected by GC.

Rection of 1 with Hydrogen. One atom of hydrogen gas was introduced into a toluene solution (20 cm^{-1}) of 1 (21.6 mg, 0.0328 mmol) at room temperature. The yellow solution gradually changed to colorless, and both ethylene (0.0086 mmol, 26%) and ethane (0.0412 mmol, 126%) were detected in the reaction vessel after 192 h. NMR analysis of the residual solid, which was obtained by evaporation of all the volatile matters, revealed the disappearance of 1 and instead the formation of $ReH_5(PMe_2Ph)_3$.[11]

Reaction of 1 with Nitrogen. Nitrogen gas was bubbled into a ether solution of 2 (34.9 mg, 0.0531 mmol) in the presence of PMe_2Ph (0.0534 mmol) for 5 h at room temperature. 2 was recovered after workup.

Reactions of $ReH_5(PMe_2Ph)_3$ with Nitrogen and Ethylene. Nitrogen gas was bubbled into an ether solution of $ReH_5(PMe_2Ph)_3$ (49.5 mg, 0.0817 mmol) in the presence of dimethylphenylphosphine (0.0843 mmol) for 5 h at room temperature. Evaporation of all the volatile matter gave the starting pentahydridorhenium complex.

Similarly, no reaction of $ReH_5(PMe_2Ph)_3$ (55.5 mg, 0.0916 mmol) with ethylene in the presence of PMe_2Ph (0.0914 mmol) for 5 h at room temperature was observed.

Reaction of 2 with Ethylene. Ethylene gas was bubbled into the toluene solution of 2 (80.5 mg, 0.105 mmol) for 7 h at room temperature. A yellow solution was obtained. Recrystallization of residual yellow solid, which was obtained by evaporation, gave

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[12] Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

[13] Katayama, C. *Acta Crystallogr.: Sect. A* **1986**, *42*, 19.

yellow crystals of 1, 30.5 mg (44%).

Reaction of 2 with Hydrogen. Hydrogen gas was bubbled into a toluene solution of 2 (80.5 mg, 0.1048 mmol) for 7 h at room temperature. After removal of toluene under vacuum, the residual solid, which was recrystallized from ether, was found to be $ReH_5(PMe_2Ph)_3$ by ^1H NMR. Yield: 0.0464 mmol, 44%. When the reaction was quenched after 4 h, a mixture of $ReH_3(PMe_2Ph)_4$[12] and $ReH_5(PMe_2Ph)_3$[11] was obtained in a ca. 1:1 ratio.

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for complexes 1 and 2 (14 pages); listings of observed and calculated structure factors for 1 and 2 (21 pages). Ordering information is given on any current masthead page.

Mechanistic Study of the Substitution Behavior of Complexes of the Type $M(CO)_5(THF)$ (M = Cr, Mo, W)

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The kinetics and mechanism of the substitution of $M(CO)_5(THF)$ (M = Cr, Mo, W) by piperidine, triethyl phosphite, and triphenylphosphine in tetrahydrofuran (THF) were studied with use of conventional and high-pressure techniques. The reactions follow the reactivity order Mo > Cr > W and are characterized by ΔH^* values between 38 and 78 kJ mol^{-1}, ΔS^* values between 0 and −120 J K^{-1} mol^{-1}, and ΔV^* values between −2 and −15 cm^3 mol^{-1}. The latter values exhibit a specific trend toward more negative values along the series Cr, Mo, and W, which is interpreted as evidence for a gradual changeover in mechanism from a more dissociative to a more associative activation process along the series of complexes.

Introduction

Our general interest in the mechanistic behavior of solventometal carbonyl complexes and their possible role in homogeneous catalysis has led us to a series of studies dealing with such species.[1-3] In general, complexes of the type $M(CO)_5S$, where S = solvent and M = Cr, Mo, and W, can be prepared either as transient species by flash photolysis techniques or as stable intermediates by conventional photochemical techniques depending on the nature of S. For weak-coordinating solvents like *n*-alkanes, benzene, toluene, and their fluorinated analogues, the $M(CO)_5S$ species are short-lived and undergo rapid substitution with the offered nucleophile. In the case of a strong-coordinating solvent like THF, it is possible to prepare pure and stable complexes of the type $M(CO)_5THF$ in solution.

The subsequent substitution reactions of $M(CO)_5S$ exhibit interesting mechanistic aspects, which caught the attention of several investigators in recent years.[4-8] Such studies usually include systematic investigations of the effect of solvent, entering ligand concentration, and temperature on the substitution process. Our earlier experience has demonstrated the difficulties involved in the assignment of the intimate nature of the substitution process based on the observed rate law and thermal activation parameters (ΔH^* and ΔS^*). The value of ΔS^* especially does not seem to be a strong indicator for the underlying mechanism in such systems.[7,8] On the basis of our earlier experience with the application of high-pressure kinetic techniques in the study of substitution reactions of metal carbonyl complexes[1,9-15], we undertook a series of flash photolysis studies[2,3] in an effort to improve our understanding of the mechanistic behavior of complexes of the type $M(CO)_5S$. In this paper we report results for M = Cr, Mo, and W, S = tetrahydrofuran (THF), and L = piperidine, PPh_3, and $P(OEt)_3$.[16] The reported data allow a systematic analysis of the influence of M and L on the underlying substitution mechanism and demonstrate a gradual changeover from a dissociative to a more associative process along the series Cr, Mo, and W.

Experimental Section

Materials. $Cr(CO)_6$ (Ventron), $Mo(CO)_6$, and $W(CO)_6$ (Riedel-de-Haen) were vacuum-sublimed before use. All solvents used were distilled and dried over Na or P_2O_5 under N_2 or Ar. Piperidine (Aldrich) was distilled over KOH under N_2. Solutions

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† Work performed at the Institute for Physical and Theoretical Chemistry, University of Frankfurt, FRG.

(1) Awad, H. H.; Dobson, G. R.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1839.

(2) Zhang, S.; Dobson, G. R.; Bajaj, H. C.; Zang, V.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3477.

(3) Zhang, S.; Zang, V.; Bajaj, H. C.; Dobson, G. R.; van Eldik, R. *J. Organomet. Chem.* **1990**, *397*, 279.

(4) Wang, L.; Zhu, X.; Spears, K. G. *J. Phys. Chem.* **1989**, *93*, 2.

(5) Oishi, S. *Organometallics* **1988**, *7*, 1237.

(6) Kalyanasundaram, K. *J. Phys. Chem.* **1988**, *92*, 2219.

(7) Schadt, M. L.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 672, and references cited therein.

(8) Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1987**, *26*, 2254, and references cited therein.

(9) Macholdt, H.-T.; van Eldik, R. *Transition Met. Chem.* **1985**, *10*, 323.

(10) Macholdt, H.-T.; van Eldik, R.; Dobson, G. R. *Inorg. Chem.* **1986**, *25*, 1914.

(11) Taube, D. J.; van Eldik, R.; Ford, P. C. *Organometallics* **1987**, *6*, 125.

(12) Schmidt, G.; Paulus, H.; van Eldik, R.; Elias, H. *Inorg. Chem.* **1988**, *27*, 3211.

(13) Awad, H. H.; Dobson, C. B.; Dobson, G. R.; Leipoldt, J. G.; Schneider, K.; van Eldik, R.; Wood, H. E. *Inorg. Chem.* **1989**, *26*, 1654.

(14) Schneider, K. J.; van Eldik, R. *Organometallics* **1990**, *9*, 1235.

(15) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(16) Wieland, S. Doctoral Thesis, University of Frankfurt, 1988.

0276-7333/91/2310-3110$02.50/0