One of the striking features of this work and previous studies dealing with the cleavage of multiple M–M bonds by isocyanides[3,36] is the rarity of isolable "intermediates" that contain these ligands bound to multiply bonded dimetal units. It seems likely that thermodynamic factors dominate, thereby leading to the electronically saturated 18-electron mononuclear species that are invariably the final products of such reactions. Interestingly, Chisholm and co-workers[37] have recently found that upon reacting the triply bonded $Mo_2(OR)_4(R'COCHCOR')_2$ complexes (R' = Me or *t*-Bu) with *tert*-butyl isocyanide, the dinuclear species $Mo_2(OR)_2(\mu\text{-}OR)_2(R'COCHCOR')_2(CN\text{-}t\text{-}Bu)_2$ are formed. It may be that the kinetic inertness of these species[37] to cleavage by excess isocyanide is related to the stability of the Mo–(β-diketonate) ring; the absence of metal–ligand dissociation can clearly stabilize these molecules to further reaction with RNC.

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Registry No. $[Re(CNPh)_6]PF_6$, 87829-81-0; $[Re(CNPh)_6][\textit{trans}\text{-}ReCl_4(CNPh)_2]$, 87829-83-2; $[Re(CN\text{-}p\text{-}tol)_6]PF_6$, 64294-09-3; $[Re(CN\text{-}p\text{-}tol)_6][\textit{trans}\text{-}ReCl_4(CN\text{-}p\text{-}tol)_2]$, 87829-85-4; $[Re(CNxylyl)_6]PF_6$, 87829-87-6; $[Re(CNxylyl)_6][\textit{trans}\text{-}ReCl_4(CNxylyl)_2]$, 87829-89-8; $[Re(CNxylyl)_6][\textit{cis}\text{-}ReCl_4(CNxylyl)_2]$, 87861-08-3; $[Re(CNxylyl)_6]_2Re_2Cl_8$, 87829-90-1; $[Re(CNmesityl)_6]PF_6$, 87829-92-3; $[Re(CNmesityl)_6][\textit{trans}\text{-}ReCl_4(CNmesityl)_2]$, 87829-94-5; $[Re(CNmesityl)_6][\textit{cis}\text{-}ReCl_4(CNmesityl)_2]$, 87861-10-7; $Re_2(O_2CCH_3)_4Cl_2$, 14126-96-6; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $ReCl_3(CNmesityl)_3$, 87829-95-6; $Re_2Cl_6(PEtPh)_2$, 55661-10-4; $Re_2H_8(PPh_3)_4$, 66984-37-0; $[Re(CNPh)_6Cl](PF_6)_2$, 87829-97-8; $[Re(CNPh)_6Br](PF_6)_2$, 87829-99-0.

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[36] Walton, R. A. *ACS Symp. Ser.* **1981**, *No. 155*, 207 and references cited therein.

[37] Chisholm, M. H.; Corning, J. F.; Folting, K.; Huffman, J. C.; Ratermann, A. L.; Rothwell, I. P.; Streib, W. E., submitted for publication.

Synthesis and Substitution Reactions of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$. The Crystal and Molecular Structure of $Mo(\eta^6\text{-}PhPMePh)(CNCMe_3)(PMePh_2)_2$

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The complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$, **1**, is readily prepared in one step by reducing a mixture of Mo_2Cl_{10} and 8 mol of $PMePh_2$ in THF with magnesium under argon. There is evidence for molybdenum complexes in oxidation states IV, II, and 0 as intermediates in the high-yield reduction process. Complex **1** reacts with 1 mol of the strongly coordinating ligands L = $P(OMe)_3$, $CNCMe_3$, and CO at 25 °C to give monosubstituted complexes $Mo(\eta^6\text{-}PhPMePh)(L)(PMePh_2)_2$, **2**–**4**, respectively. Use of excess ligand results in disubstituted products. Only ligands that are sterically smaller than $PMePh_2$ including N_2, PMe_2Ph, PMe_3, and C_2H_2 react with **1**; PPh_3 and $P(C_6H_{11})_3$ do not react. Carbon monoxide uptake kinetics indicate that dissociation of a σ-bonded ligand from **1** is the rate-determining step for these reactions; rate = $k_1[\mathbf{1}]$, $k_1(303\ K) = (1.5 \pm 0.1) \times 10^{-3}\ s^{-1}$, $\Delta H^* = 28.8 \pm 1.6$ kcal mol^{-1}, and $\Delta S^* = 23 \pm 5$ eu. The σ-bonded $PMePh_2$ ligands in **2**–**4** are diastereotopic and give ABX or AB ^{31}P NMR spectra. The ^{31}P chemical shift of the η^6-PhPMePh ligand is sensitive to the electronic and/or steric properties of the σ-bonded ligands. Compound **3**, $Mo(\eta^6\text{-}PhPMePh)(CNCMe_3)(PMePh_2)_2$, has been studied by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1$ with cell dimensions $a = 9.256$ (3) Å, $b = 11.497$ (3) Å, $c = 18.782$ (10) Å, $\beta = 103.92$ (4)°, $V = 1940$ $Å^3$, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 2$. The structure was solved by the heavy-atom method and refined by least-squares and Fourier methods to final residuals $R = 0.0635$ ($R_w = 0.0785$) for 2755 observed ($I > 2\sigma(I)$) reflections. The geometry about the molybdenum is distorted octahedral. Principal dimensions are Mo–P = 2.416 (3) and 2.420 (3) Å, Mo–C(isocyanide) = 1.984 (13) Å, and Mo–C(arene) = 2.24 (1)–2.32 (1) Å. Angles in the $MoP_2(CNCMe_3)$ tripod indicate that the bulky phosphines have moved from ideal octahedral positions toward the $CNCMe_3$ ligand to minimize steric repulsions. The $CNCMe_3$ ligand is nonlinear (C–N–C = 150 (1)°) and is the closest ligand in the tripod to the PMePh group on the η^6 ring.

Introduction

The complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (**1**)[1] is an unusual member of the class of compounds $Mo(\eta^6\text{-}arene)(PR_3)_3$ first synthesized by Green and Silverthorn.[2] Its preparation (eq 1) is the simplest yet described for such

$$Mo_2Cl_{10} + 8PMePh_2 + 5Mg \xrightarrow[THF]{Ar} 2\,\mathbf{1} + 5MgCl_2 \quad (1)$$

complexes,[2,3] and it appears to be unique in containing labile σ-bonded ligands that are substituted by a range of

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[1] Azizian, H.; Luck, R.; Morris, R. H.; Wong, H. *J. Organomet. Chem.* **1982**, *238*, C24.

[2] (a) Green, M. L. H. *J. Organomet. Chem.* **1980**, *200*, 119. (b) Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2164. (c) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *Ibid.* **1974**, 1361. (d) Green, M. L. H.; Silverthorn, W. E. *Ibid.* **1973**, 301. (e) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc. A* **1971**, 2929.

[3] (a) Davies, M. C.; George, T. A. *J. Organomet. Chem.* **1982**, *224*, C25. (b) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639. (c) Mason, R.; Thomas, K. M.; Heath, G. A. *J. Organomet. Chem.* **1975**, *90*, 195.

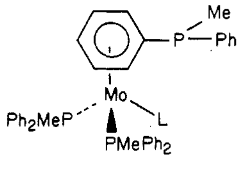
0276-7333/84/2303-0247$01.50/0

Table I. NMR Data for Complexes $Mo(\eta^6\text{-}PhPMePh)(L)(PMePh_2)_2$, 1-5, in C_6D_6

	^{31}P NMR[a]			^1H NMR						
		P-Mo		$CH_3P\text{-}\eta^6\text{-}Ph$		$CH_3P\text{-}Mo$			L	
complex (L)	$P\text{-}\eta^6\text{-}Ph$, ppm	δ_A,δ_B, ppm	J_{AB}, Hz	δ	J_{PH}, Hz	δ	J_{PH}, Hz	$\eta^6\text{-}C_6H_5$, δ	δ	J, Hz
1 ($PMePh_2$)	−31.0	34.1	0	1.20	5	1.77 (br)		3.55, 3.67 (o) 4.13, 4.13 (m) 4.40 (p)		
2 ($P(OMe)_3$)	−27.9	40.2[b,c] 38.9[b,d]	31 31	1.42	4	1.84 1.92	5 5	3.50, 3.64 (o)[e] 4.37, 4.37 (m)[e] 4.53 (p)[e]	3.30[f]	10
3 ($CNCMe_3$)	−24.1	38.4[g] 38.1[g]	29 29	1.50	4	1.59 1.77	5 5	3.70, 4.34 (o)[e] 3.99, 4.07 (m)[e] 4.20 (p)[e]	1.40	
4 (CO)	−23.2	40.3[g] 39.6[g]	30 30	1.57	5	1.69 1.72	4 4	3.6, 3.9 4.2, 4.3 4.3		
5 (N_2)	−24.8	35.1[g] 34.4[g]	28 28	1.47	5	1.61 1.63	4 4	3.3, 3.5 3.92 3.86		

[a] These data are more accurate than those of ref 1. [b] ABX spin system, δ_X 176.3 ($P(OMe)_3$). [c] J_{AX} = 52 Hz. [d] J_{BX} = 55 Hz. [e] Multiplets assigned by decoupling; o = ortho, m = meta, p = para. [f] Doublet. [g] AB spin system.

ligands at 25 °C to give complexes that include 2,[1] 3, and 4. It reacts reversibly with dinitrogen to give complex 5[4]



1, L = $PMePh_2$
2, L = $P(OMe)_3$
3, L = $CNCMe_3$
4, L = CO
5, L = N_2

and with dihydrogen to give the dihydride $Mo(\eta^6\text{-}PhPMePh)(H)_2(PMePh_2)_2$.[4] Related electron-rich monosubstituted complexes have been tested as reductants of dinitrogen[2a,b] and carbon monoxide[5] and as catalysts for the hydrogenation of arenes.[6] In addition complexes containing η^6-bonded arylphosphine ligands including complexes 2, 3, and $Mo(\eta^6\text{-}PhPMePh)(dppe)(PMePh_2)$ (6)[7a] can serve as phosphine-like ligands to build up novel bi- and trimetallic compounds.[7] Here we consider the reasons for the formation of complex 1 and the nature of its substitution reactions with strongly coordinating ligands.

Experimental Section

General Data. All reactions were conducted under an inert-atmosphere of nitrogen, argon, or vacuum as appropriate. Solids were handled under nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-1 drytrain. Solvents apart from methanol were dried over sodium–benzophenone ketyl and distilled under nitrogen. Tetrahydrofuran (THF) was redistilled from lithium aluminum hydride. Methanol was dried over and distilled from magnesium methoxide. $PMePh_2$, $P(OMe)_3$, dppe ($PPh_2CH_2CH_2PPh_2$), and $CNCMe_3$ were used as received from Strem Chemical Co. Complete and improved syntheses of complexes 1 and 2[1] are reported below.

NMR spectra were recorded by using a Bruker WP 80 and a Varian XL-200 spectrometer. ^{31}P chemical shifts were measured relative to $P(OMe)_3$ (1% in C_6D_6) in an insert tube but are reported relative to 85% H_3PO_4 with the use of $\delta(P(OMe)_3)$ +140.7 ppm. A Unicam SP 1025 provided IR spectra. Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver.

Preparation of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (1). Molybdenum pentachloride ($^1/_2Mo_2Cl_{10}$, 0.65 g, 2.38 mmol) was dissolved in a solution of methyldiphenylphosphine (2.40 g, 11.9 mmol) in rigorously dry THF (50 mL) under argon. Excess Grignard magnesium (1.2 g, 49 mmol) activated by exposure to iodine vapor was then rapidly added with vigorous stirring. The reaction solution turned from red to green after ca. 10 min and then rapidly turned red-brown. The brown solution that is very sensitive to dinitrogen as well as dioxygen was allowed to stir for 30 min. Magnesium was filtered off by using a coarse porosity frit. The filtrate was concentrated to 15 mL and treated dropwise with 15 mL of methanol to yield an orange, oxygen-sensitive powder which was washed with methanol (3 × 5 mL) and dried in vacuo at 25 °C. The product was recrystallized under argon from benzene/methanol and dried for 12 h at 10^{-3} torr, 25 °C (1.55 g, 75%). Anal. Calcd for $C_{52}H_{52}MoP_4$: C, 69.64; H, 5.84. Found: C, 69.20; H, 6.01. Low carbon analyses were also obtained on samples that were recrystallized in the presence of added ligand[1] and were shown to not contain detectable amounts of chloride. The problem may be due to incomplete combustion of carbon. If nitrogen is not excluded during recrystallization, then complex 1 is contaminated by traces of complex 5,[4] previously thought to be an oligomeric substance.[1]

Preparation of $Mo(\eta^6\text{-}PhPMePh)(P(OMe)_3)(PMePh_2)_2$ (2). Trimethyl phosphite (20 mg, 0.16 mmol) was added dropwise from a 50-μL syringe to a solution of complex 1 (0.10 g, 0.11 mmol) in 15 mL of THF. After 1 h of stirring the volume was reduced under vacuum to 2 mL and cold methanol (2 mL) was added slowly to precipitate the yellow-orange microcrystalline product (72 mg, 80%) without separating out oils containing excess $PMePh_2$. The product was washed with cold methanol (5 × 2 mL), recrystallized from THF/MeOH, and dried under high vacuum: yield 68 mg (75%); ^1H and ^{31}P NMR, see Table I. Anal. Calcd for $C_{42}H_{48}MoP_4O_3$: C, 61.47; H, 5.90. Found: C, 61.34; H, 5.76.

Preparation of $Mo(\eta^6\text{-}PhPMePh)(CNCMe_3)(PMePh_2)_2$ (3). Orange crystals of this compound were obtained by reacting compound 1 with 1 equiv of *tert*-butyl isocyanide according to the synthesis and recrystallization procedure for making 2: yield 70%; see Table I for ^1H and ^{31}P NMR data; ^{13}C NMR (C_6D_6) δ 207.3 (s, 1, C≡N), 148–141 (m, $J_{CP} \approx 25$ Hz, 5, CP of MoPPh),

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(4) Luck, R.; Morris, R. H. *Inorg. Chem.*, in press.

(5) (a) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1139. (b) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona-Guzman, E.; Wilkinson, G. *Ibid.* **1979**, 1519.

(6) Muetterties, E. L.; Schaeffer, H.; Mink, R. I.; Darensbourg, M. Y.; Millar, M.; Groshens, T.; Klabunde, K. J. *Inorg. Chem.* **1979**, *18*, 883.

(7) (a) Luck, R.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221. (b) Alyea, E. C.; Ferguson, G.; Somogyvari, A. *Organometallics* **1983**, *2*, 668. (c) Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *60*, C11. (d) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1973**, *26*, 43. (e) Wasserman, H. J.; Wovkulich, M. J.; Atwood, J. D.; Churchill, M. R. *Inorg. Chem.* **1980**, *19*, 2831. (f) Faggiani, R.; Hao, N.; Lock, C. J. L.; Sayer, B. G..; McGlinchey, M. J. *Organometallics* **1983**, *2*, 96.

Table II. First-Order Rate Constants (k) for the Dissociation of Mo(η^6-PhPMePh)($PMePh_2$)$_3$, 1, in Toluene Solution as a Function of Temperature (T) as Determined by Carbon Monoxide Uptake at Pressure P

run	T, K	10^2[1], M	P(CO), torr	10^3k, s^{-1}
1	294.0	0.67	371	0.30
2	295.0	1.38	371	0.38
3	297.0	1.35	371	0.67
4[a]	303.2	0.66	371	1.6
5	303.5	2.68	702	1.6
6	303.5	0.67	703	2.0
7	304.1	1.36	513	1.7
8	306.4	0.67	703	2.1
9	307.0	1.34	373	2.9
10[b]	306	3.28	b	2.3

[a] [$PMePh_2$] = 6.7×10^{-3}. [b] Rate determination of the reaction of *tert*-butyl isocyanide (3.28×10^{-2} M) with complex 1 in benzene by ^{31}P NMR.

135–127 (m, 25, *o*-C, *m*-C, *p*-C of MoPPh), 83.6 (d, J_{CP} = 31 Hz, 1, CP of η^6-Ph), 83.1, 80.4, 80.3, 78.3, 76.1 (each a singlet, 5, *o*-C, *m*-C, *p*-C of η^6-Ph), 56.1 (s, 1, N*C*Me$_3$), 31.9 (s, 3, C(CH_3)$_3$), 20.9 (d, J_{CP} = 17 Hz, PCH_3), 17.5 (d, J_{CP} = 17 Hz, 1, PCH_3), 11.9 (d, J_{CP} = 15.5 Hz, 1, η^6-PhP*C*H_3); IR (benzene) 1940 cm^{-1} (s, br, $\Delta\nu$ = 200 cm^{-1}, CN). Anal. Calcd for $C_{44}H_{48}NMoP_3$: C, 67.78; H, 6.21; N, 1.80. Found: C, 67.74; H, 6.24; N, 1.75.

Reaction of 1 with Carbon Monoxide. Gas-Uptake Kinetics. The rate of the reaction of 1 (0.6–3.3 M) in toluene with carbon monoxide (370–703 torr) was monitored over a range of temperatures (21–34 °C) by using a constant pressure, gas-uptake apparatus.[4,8] In a typical run, complex 1 (60 mg) was suspended in a glass bucket over 10 mL of toluene. The solvent was freeze–thaw degassed and then equilibrated with carbon monoxide at the required pressure and temperature. Solid 1 does not react with CO over this time period. The bucket was dropped, the flask was rapidly shaken, and the rate of uptake was measured over 1 half-life of reaction. Plots of log V, where V is the uptake volume, vs. time were linear over this region and yielded rate constants ($k \pm 16\%$,[9] Table II) that were independent of the CO pressure as expected for a first-order reaction producing the complex Mo(η^6-PhPMePh)(CO)($PMePh_2$)$_2$ (4), ν(CO) = 1830 cm^{-1} (benzene). After 1 half-life plots deviate from linearity because of extra gas uptake corresponding to the formation of a dicarbonyl product (ν(CO) = 1900 cm^{-1}, 1830 cm^{-1}). Attempts to selectively precipitate complex 4 using methanol at the onset of dicarbonyl formation or at an uptake ratio CO/Mo = 1.0 yielded inseparable mixtures (yield 60%) of 4 (>80%), 1, and some dicarbonyl product. Complex 4 was characterized in solution by IR and NMR methods (Table I).

Reactions with Other Ligands. Dinitrogen. Complex 1 in solution takes up ~0.34 mol N_2 to give an equilibrium mixture containing 1, $PMePh_2$, and Mo(η^6-PhPMePh)(N_2)($PMePh_2$)$_2$, (5); see ref 4: IR (benzene) 1980 cm^{-1} (w, NN); NMR, see Table I.

Acetonitrile. A thermally unstable, red-brown complex Mo(η^6-PhPMePh)(NCMe)($PMePh_2$)$_2$ was obtained by stirring complex 1 as a suspension in acetonitrile and filtering off the product after 4 h. It decomposes when dry: IR (Nujol) 2170 cm^{-1} (s, CN).

Trimethylphosphine. Addition of 1 equiv of PMe_3 to complex 1 gives free $PMePh_2$ and Mo(η^6-PhPMePh)(PMe_3)($PMePh_2$)$_2$ as the only product as indicated by ^{31}P NMR (benzene): δ −30.2 (s, 1, P–η^6-Ph), 37.3 A, 36.3 B (ABX system, J_{AB} = 30 Hz, J_{AX} = 29, J_{BX} = 34 Hz, 2, MoPMePh$_2$), −4.4 X (ABX system, ddd, J_{AX}, J_{BX} as above, J(X,P–η^6-Ph) = 6 Hz, 1, PMe_3).

Dimethylphenylphosphine. Mo(η^6-PhPMePh)(PMe_2Ph)($PMePh_2$)$_2$ was observed as above by ^{31}P NMR (benzene): δ −30.0 (s, 1, P–η^6-Ph), 37.3 A, 36.7 B (ABX system, J_{AB} = 28, J_{AX} = 30, J_{BX} = 30 Hz, 2, MoPMePh$_2$), 11.3 X (ABX system, t, J_{AX}, J_{BX} as above, 1, PMe_2Ph).

Table III. Crystal Data and Details of Intensity Measurements

compd	$C_{44}H_{48}MoNP_3$
system	monoclinic
a, Å	9.256 (3)
b, Å	11.497 (3)
c, Å	18.782 (10)
β, deg	103.92 (4)
V, Å^3	1940
fw	779.7
Z	2
D_{calcd}, g cm^{-3}	1.33
space group	$P2_1$ (by analysis)
μ(Mo K$\bar{\alpha}$), cm^{-1}	4.8
T, °C	25
reflctns used in cell determination no./range in θ	22/(4.9 < θ < 11.9)
cryst dimens, cm	thin plate {001}: 0.0019 {100}: 0.0138 {010}: 0.0175
scan mode	θ:2θ
scan width	0.90 + 0.35 tan θ
max scan time, s	80
std reflctns (no./interval in s)	3/12000
max 2θ, deg	50
prescan rate, deg min^{-1}	10
acceptance ratio, $\sigma(I)/I$	0.04
total reflctns collected	4007
unique data	3512

Acetylene. Complex 1 in toluene at 25 °C takes up 2.5 mol of gas (1 atm) to give a black solution and a small amount amount of black solid. Anal. Found: C, 46.23; H, 4.75.

Crystallographic Analysis of Complex 3. Red crystals as thin plates were obtained by slow evaporation of a MeOH/THF (ratio 2.0) mixture saturated with complex 3. Crystals were wedged into 0.2–0.3 mm Lindemann capillaries and sealed under nitrogen. The crystal used in the data collection had dimensions 0.350 × 0.275 × 0.050 mm in the *a*, *b*, and *c* directions, respectively. Precession photographs were used to obtain preliminary cell and symmetry information. Further work on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å) gave the crystal data summarized in Table III. Cell constants were obtained by least-squares refinement of the setting angles of 22 reflections within the θ range specified. The conditions for data collection are given in Table III. For each reflection backgrounds were measured by extending the scan by 25% on either side of the peak and were measured for half the time taken to collect the peak. All reflections in the quadrants ($h,k,\pm l$) with $2\theta \leq 50°$ were measured, and repeat measurements of three standard reflections showed no systematic variations. After Lorentz and polarization corrections were applied, equivalent reflections were averaged and systematically absent reflections were excluded; this left 3512 unique reflections.

The acentric space group $P2_1$ was assumed on the basis of the value of Z = 2 and was used throughout. The structure was routinely solved by the use of the Patterson function to locate the Mo atom. All other atoms were then located after several cycles of least-squares and Fourier calculations, and in the final cycles hydrogen atoms attached to the phenyl rings were placed in calculated positions (C–H = 0.95 Å) with fixed temperature factors B = 6.0 Å^2 but were not refined. Full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$ then converged (maximum shift/error = 0.04) to final agreement indices R = 0.0635 (R_w = 0.0785) for 2755 reflections with $I > 2\sigma(I)$. In the final cycle weights were given by $w = 4F^2\{\sigma(I)^2 + (0.12F^2)^2\}^{-1}$ and, at convergence, the esd of an observation of unit weight was 1.109. The final difference Fourier contained as its major features several residual peaks up to 1.46 e Å^{-3} in height within 1 Å of the Mo atom. The alternative "hand" of the crystal was not refined. A PDP 11/23 computer and programs in the Enraf-Nonius SDP package were used for the refinements.

Final positional parameters and selected bond lengths and bond angles are given in Tables IV and V. Tables VI–X containing bond lengths and bond angles for the phenyl rings, thermal pa-

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(8) Chalk, A. J.; Halpern, J. *J. Am. Chem. Soc.* **1959**, *81*, 5846.

(9) The large error results from difficulties in handling air-sensitive complex 1 and in measuring the rates at the higher temperatures by using this method.

Table IV. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å²
Mo	0.22927 (8)	0.250	0.24292 (5)	2.13 (1)
P1	0.3426 (3)	0.1292 (3)	0.1658 (2)	2.31 (6)
P2	0.3001 (3)	0.1229 (3)	0.3481 (2)	2.74 (6)
P3	0.1513 (4)	0.5099 (3)	0.1109 (2)	3.27 (7)
N1	0.552 (1)	0.360 (1)	0.3087 (6)	3.8 (2)
C1	0.219 (1)	0.040 (1)	0.0949 (8)	4.1 (3)
C2	0.499 (1)	0.110 (1)	0.3981 (7)	4.4 (3)
C3	0.307 (1)	0.591 (1)	0.1687 (9)	5.0 (4)
C4	0.427 (1)	0.321 (1)	0.2840 (6)	2.6 (2)
C5	0.646 (1)	0.451 (1)	0.3474 (7)	3.4 (3)
C6	0.761 (2)	0.387 (2)	0.4041 (8)	5.4 (4)
C7	0.558 (2)	0.533 (1)	0.3811 (9)	5.1 (4)
C8	0.725 (2)	0.509 (1)	0.2946 (9)	5.2 (4)
C11	0.476 (1)	0.019 (1)	0.2103 (6)	3.1 (3)
C12	0.438 (1)	−0.096 (1)	0.2150 (7)	3.7 (3)
C13	0.552 (2)	−0.176 (1)	0.2541 (9)	5.2 (4)
C14	0.689 (2)	−0.140 (2)	0.2837 (8)	5.2 (4)
C15	0.725 (1)	−0.028 (1)	0.2774 (8)	4.0 (3)
C16	0.627 (1)	0.051 (1)	0.2427 (7)	3.6 (3)
C21	0.455 (1)	0.195 (1)	0.1081 (6)	3.0 (2)
C22	0.534 (2)	0.128 (1)	0.0685 (7)	4.6 (3)
C23	0.622 (2)	0.176 (2)	0.0296 (8)	5.9 (4)
C24	0.634 (2)	0.295 (2)	0.0277 (7)	5.3 (4)
C25	0.565 (2)	0.363 (2)	0.0659 (8)	5.3 (4)
C26	0.471 (1)	0.314 (1)	0.1053 (7)	3.7 (3)
C31	0.224 (1)	0.174 (1)	0.4225 (6)	2.9 (3)
C32	0.284 (1)	0.270 (2)	0.4618 (7)	4.8 (3)
C33	0.227 (2)	0.319 (1)	0.5154 (9)	5.7 (4)
C34	0.094 (2)	0.269 (1)	0.5310 (7)	5.1 (3)
C35	0.038 (1)	0.174 (2)	0.4945 (7)	4.6 (3)
C36	0.098 (1)	0.124 (1)	0.4407 (7)	4.0 (3)
C41	0.242 (1)	−0.029 (1)	0.3429 (6)	3.1 (3)
C42	0.128 (1)	−0.066 (1)	0.2846 (7)	3.9 (3)
C43	0.078 (2)	−0.179 (1)	0.2780 (8)	5.1 (3)
C44	0.137 (2)	−0.260 (1)	0.3292 (7)	5.4 (3)
C45	0.257 (2)	−0.225 (1)	0.3865 (9)	6.1 (4)
C46	0.302 (2)	−0.109 (1)	0.3943 (7)	4.4 (3)
C51	0.108 (1)	0.403 (1)	0.1726 (6)	2.7 (2)
C52	0.044 (1)	0.301 (1)	0.1446 (7)	3.3 (3)
C53	−0.017 (1)	0.217 (1)	0.1868 (8)	4.0 (3)
C54	−0.005 (1)	0.240 (1)	0.2603 (6)	3.8 (3)
C55	0.061 (1)	0.345 (1)	0.2912 (6)	3.6 (3)
C56	0.118 (1)	0.422 (1)	0.2482 (7)	3.2 (3)
C61	0.002 (1)	0.617 (1)	0.1079 (6)	3.0 (3)
C62	−0.127 (1)	0.591 (1)	0.1266 (8)	4.0 (3)
C63	−0.243 (2)	0.674 (2)	0.1173 (8)	5.2 (4)
C64	−0.227 (2)	0.781 (1)	0.0907 (9)	5.7 (4)
C65	−0.095 (2)	0.806 (1)	0.0691 (9)	6.0 (4)
C66	0.016 (1)	0.726 (1)	0.0789 (8)	4.3 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)\}$.

rameters, least-squares mean planes, root-mean-square vibration amplitudes, and final structure amplitudes have been deposited as supplementary material.

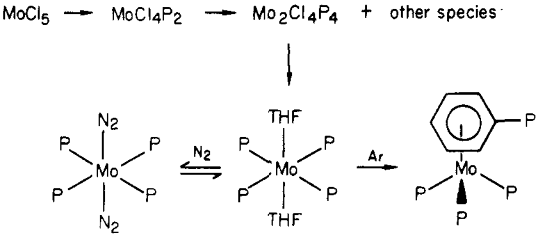
Results and Discussion

Synthesis of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (1). We first identified this compound as a side product in the preparation of $Mo(N_2)_2(PMePh_2)_4$ by the reduction of molybdenum pentachloride with Grignard magnesium in a dry tetrahydrofuran (THF) solution of methyldiphenylphosphine under a nitrogen atmosphere (eq 2).[1] If

$$Mo_2Cl_{10} + 8PMePh_2 + 5Mg \xrightarrow[\text{THF}]{N_2} \underset{70\%}{Mo(N_2)_2(PMePh_2)_4} + \underset{20\%}{1} + 5MgCl_2 \quad (2)$$

the reduction is conducted under argon, then only 1 is obtained (eq 1). It can be precipitated directly from the reaction solution as an orange, oxygen-sensitive solid by addition of methanol; this method eliminates a benzene extraction step suggested previously[1] that is necessary in the case of reaction 2 for the isolation of $Mo(N_2)_2(PMePh_2)_4$ free from 1 by fractional crystallization.[10,11]

Scheme I. Common Intermediates of Reactions 1 and 2



Benzene solutions of 1 under argon give characteristic singlets in the ^{31}P NMR spectrum at 34.1 ppm for the σ-bonded ligands, equivalent because of rotation of the π-bonded ring, and −31.0 ppm for the "dangling" phosphorus (Table I). The noteable features of the ^1H spectrum (Table I) are the multiplets due to protons on the η^6-bonded arene in the region δ 3.5–4.4 and the two methyl resonances at δ 1.77 (σ-bonded ligands) and 1.20 (η^6-bonded ligand); these have been discussed elsewhere.[1] When solutions of 1 are placed under nitrogen, then small amounts of the dinitrogen complex 5 and free $PMePh_2$ form; this accounts for most of the resonances in the ^1H NMR spectrum previously assigned to oligomeric impurities that were thought to form from 1.[1]

The courses of the two reduction reactions 1 and 2 are complex, but certain intermediates are common to both. The solutions turn red when the molybdenum pentachloride, magnesium, and phosphine are first mixed suggesting the formation of $MoCl_4(PMePh_2)_2$.[12] After 10–15 min the solutions turn green and ^{31}P NMR spectra recorded at this stage show a resonance at 6.0 ppm attributable to intensely green $Mo_2Cl_4(PMePh_2)_4$, (μ-Mo$\overset{4}{-}$Mo),[13] along with other peaks. This dimer is indeed a good precursor to molybdenum(0) dinitrogen complexes.[14] Finally the solutions turn a deep orange-brown colour from which the products are isolated. It is at the brown stage that dinitrogen uptake is observed during the formation of $Mo(N_2)_2(PMePh_2)_4$ and it may be at this time that an intermediate capable of coordinating arenes is produced.

There is circumstantial evidence that this intermediate is a solvated tetrakis(phosphine)molybdenum(0) species (Scheme I). For example, the preparation of 1 can be conducted by using a benzene/THF solvent mixture with no detectable formation of the known, insoluble complex $Mo(\eta^6\text{-}C_6H_6)(PMePh_2)_3$.[2e] Complex 1 is obtained in 50% yield by heating $Mo(N_2)_2(PMePh_2)_4$ in toluene in vacuo.[15] Similarly $Mo(N_2)_2(PMePh_2)_3(NC_5H_5)$ in toluene gives the π-pyridine complex $Mo(\eta^6\text{-}NC_5H_5)(PMePh_2)_3$ and none of the toluene π complex.[15] The π complexes cannot be converted back to the dinitrogen complexes. Such a four-phosphine intermediate was observed in a flash photolysis study of $W(N_2)_2(dppe)_2$.[16] Also a brown solution thought to contain solvated $Mo(PMe_2Ph)_4$ was re-

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[10] Morris, R. H.; Luck, R.; Ressner, J. M., to be submitted for publication.

[11] George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678.

[12] Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652.

[13] Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1716.

[14] Green, M. L. H., personal communication.

[15] Morris, R. H.; Ressner, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 909.

[16] Thomas, R. J. W.; Laurence, G. S.; Diamantis, A. A. *Inorg. Chim. Acta Lett.* **1978**, *30*, L353.

Table V. Selected Distances (A) and Bond Angles (deg) for Complex 3[a]

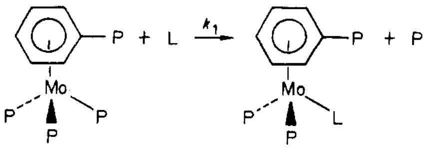
atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	P1	2.420 (3)	Mo	C56	2.244 (12)	P3	C51	1.802 (13)
Mo	P2	2.416 (3)	P1	C1	1.848 (13)	P3	C61	1.842 (12)
Mo	C4	1.984 (13)	P1	C11	1.827 (13)	N1	C4	1.222 (15)
Mo	C51	2.319 (11)	P1	C21	1.834 (15)	N1	C5	1.44 (2)
Mo	C52	2.272 (12)	P2	C2	1.863 (12)	C5	C6	1.51 (2)
Mo	C53	2.302 (11)	P2	C31	1.806 (12)	C5	C7	1.48 (2)
Mo	C54	2.274 (10)	P2	C41	1.828 (14)	C5	C8	1.52 (2)
Mo	C55	2.262 (13)	P3	C3	1.836 (15)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P1	Mo	P2	94.0 (1)	C53	Mo	C55	64.0 (5)	Mo	C51	P3	136.9 (6)
P1	Mo	C4	88.5 (3)	C53	Mo	C56	75.6 (5)	Mo	C51	C52	70.9 (7)
P1	Mo	C51	108.4 (3)	C54	Mo	C55	36.4 (6)	Mo	C51	C56	69.1 (6)
P1	Mo	C52	90.7 (4)	C54	Mo	C56	64.8 (6)	P3	C51	C52	119 (1)
P1	Mo	C53	98.9 (4)	C55	Mo	C56	35.7 (5)	P3	C51	C56	124 (1)
P1	Mo	C54	128.5 (5)	Mo	P1	C1	117.8 (5)	C52	C51	C56	116 (1)
P1	Mo	C55	163.0 (4)	Mo	P1	C11	117.9 (4)				
P1	Mo	C56	143.4 (4)	Mo	P1	C21	120.5 (5)	Mo	C52	C51	74.7 (7)
P2	Mo	C4	83.5 (3)	C1	P1	C11	100.1 (6)	Mo	C52	C53	72.6 (7)
P2	Mo	C51	157.2 (3)	C1	P1	C21	98.4 (7)	C51	C52	C53	124 (1)
P2	Mo	C52	145.4 (4)	C11	P1	C21	98.0 (7)	Mo	C53	C52	70.3 (6)
P2	Mo	C53	108.5 (4)	Mo	P2	C2	120.2 (5)	Mo	C53	C54	71.3 (6)
P2	Mo	C54	86.1 (4)	Mo	P2	C31	110.9 (4)	C52	C53	C54	118 (1)
P2	Mo	C55	92.4 (3)	Mo	P2	C41	121.2 (4)	Mo	C54	C53	73.6 (7)
P2	Mo	C56	122.3 (4)	C2	P2	C31	99.2 (6)	Mo	C54	C55	71.3 (7)
C4	Mo	C51	100.8 (5)	C2	P2	C41	101.0 (7)	C53	C54	C55	120 (1)
C4	Mo	C52	131.0 (5)	C31	P2	C41	100.7 (6)	Mo	C55	C54	72.3 (8)
C4	Mo	C53	165.2 (5)	C3	P3	C51	103.5 (7)	Mo	C55	C56	71.5 (7)
C4	Mo	C54	142.3 (6)	C3	P3	C61	98.9 (7)	C54	C55	C56	120 (1)
C4	Mo	C55	107.9 (5)	C51	P3	C61	101.1 (6)	Mo	C56	C51	74.8 (7)
C4	Mo	C56	90.8 (5)	C4	N1	C5	150 (1)	Mo	C56	C55	72.8 (8)
C51	Mo	C52	34.4 (5)	Mo	C4	N1	178 (1)				
C51	Mo	C53	64.8 (5)	N1	C5	C6	104 (1)				
C51	Mo	C54	76.8 (5)	N1	C5	C7	110 (1)				
C51	Mo	C55	64.9 (5)	N1	C5	C8	108 (1)				
C51	Mo	C56	36.1 (5)	C6	C5	C7	112 (1)				
C52	Mo	C53	37.0 (5)	C6	C5	C8	108 (1)				
C52	Mo	C54	64.6 (5)	C7	C5	C8	114 (1)				
C52	Mo	C55	75.2 (5)								
C52	Mo	C56	62.9 (5)								
C53	Mo	C54	35.1 (5)								

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

ported to give a bis(dinitrogen) complex under nitrogen and in some cases an η^6-bonded phosphine complex Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ under argon.[3b] The η^6 complexation of other arylphosphine ligands to give Mo(η^6-4-$CH_3OC_6H_4P(C_6H_4OCH_3\text{-}4)_2$(triphos)[3a] and Mo($\eta^6$-PhPMePh)(dppe)(PMePh$_2$) (**6**)[7a] also likely proceeds through sterically strained intermediates containing four bulky, σ-bonded ligands. The σ to π rearrangement depicted in Scheme I would relieve this strain and would explain why arene solvents cannot compete for coordination sites on the intermediates.

Synthesis of Complexes Mo(η^6-PhPMePh)(L)(PMePh$_2$)$_2$. Complex **1** reacts with 1 equiv of the small ligands P(OMe)$_3$ and CNCMe$_3$ at 25 °C to give after workup the monosubstituted products **2** and **3**, respectively, as analytically pure, orange, air-sensitive crystals (eq 3). Their spectroscopic properties are listed in Table I, and the crystal structure of **3** has been determined. Other small, strongly coordinating ligands such as carbon monoxide, trimethylphosphine, and dimethylphenylphosphine give monosubstituted complexes that have been characterized in solution. Disubstituted complexes Mo(η^6-PhPMePh)(L)$_2$(PMePh$_2$) form if an excess of the phosphorus donor ligands is added (NMR evidence[10]). In this way the complex **6** has been prepared from the reaction of **1** with dppe.[7a] A dicarbonyl complex forms in the carbon monoxide reaction and prevents the isolation of complex **4** in a pure form. Acetylene also rapidly displaces more than one σ-bonded ligand from **1** to give a black insoluble precipitate of unknown structure. At the other extreme dinitrogen, a weakly coordinating ligand, gives an equilibrium mixture of complex **1** and the dinitrogen complex **5**.[4]



(3)

All of the ligands discussed so far have cone angles[17] smaller than that of methyldiphenylphosphine (136°): dppe (125°), PMe$_2$Ph (122°), PMe$_3$ (107°), CNCMe$_3$ (~100°), CO (~95°), N$_2$ (~95°). Ligands with larger cone angles such as triphenylphosphine (145°) and tricyclohexylphosphine (170°) do not react with **1** (NMR evidence) even though they bond strongly to other molybdenum(0) centers. Thus there are steric restrictions for reaction 3, and this accords with a dissociative substitution mechanism (see below).

NMR Spectra. A signature of each of the complexes is its ^{31}P NMR resonance (Table I) for the "dangling" phosphorus atom (P–η^6-Ph) whose chemical shift is near that of uncoordinated PMePh$_2$ at −27.7 ppm. The chemical shifts of ^{31}P nuclei in phosphines are sensitive to both

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[17] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

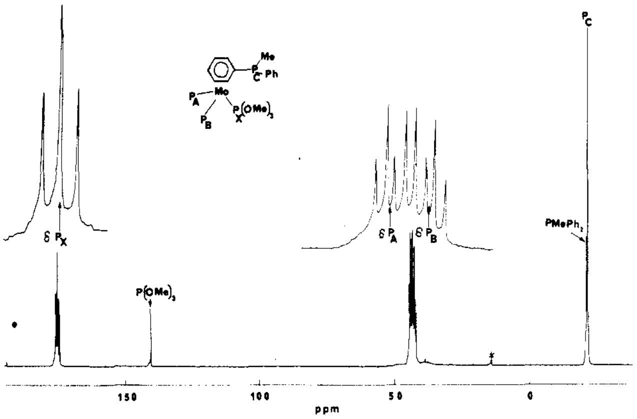

Figure 1. The ^{31}P NMR spectrum at 81 MHz of Mo(η^6-PhPMePh)(P(OMe)$_3$)(PMePh$_2$)$_2$ in C_6H_6 showing the ABX spin system. The peaks at 140.4 and −27.7 ppm (shoulder) are reference compounds of P(OMe)$_3$ and PMePh$_2$, respectively.

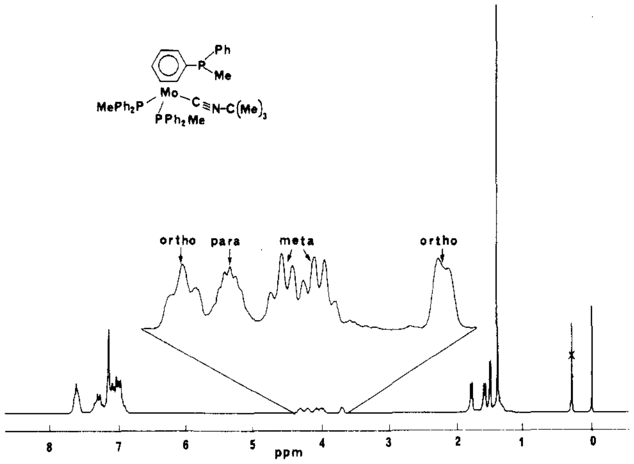

Figure 2. The 200-MHz ^1H spectrum of Mo(η^6-PhPMePh)(CNCMe$_3$)(PMePh$_2$)$_2$ in C_6D_6 showing the assignment of η^6-arene protons as determined by decoupling methods.

the size and electronegativity of the substituents attached to them.[17,18] Here the chemical shifts are observed to increase roughly as the electronegativity of the substituents on the molybdenum (as determined by their σ donor to π acceptor ratios or Tolman's electronic parameter[17]) decrease with the exception of PMePh$_2$: δ −31.0 (PMePh$_2$) < −30.2 (PMe$_3$) < −30.0 (PMe$_2$Ph) < −28.0 (complex 6)[7a] < −27.9 (P(OMe)$_3$) < −24.8 (N$_2$) < −24.1 (CNCMe$_3$) < −23.2 (CO). However, these chemical shifts also correlate with the ligand sizes or cone angles,[17] increasing as the sizes decrease apart from those for PMe$_3$ and CNCMe$_3$. Thus at present it is not possible to unambiguously distinguish between electronic and steric influences on these chemical shifts.

A common feature of the NMR spectra (Table I) is the occurrence of diastereotopic nuclei (^1H, ^{31}P) resulting from the chiral center on the η^6-bonded phosphine ligand. The inequivalent σ-bonded methyldiphenylphosphines in complexes 3–5 give AB-type ^{31}P resonances at 81 MHz. Compound 2 shows additional coupling to the phosphite resonance resulting in an ABX spin system (Figure 1). In the ^1H NMR spectra, the methyl groups of these ligands are also seen to be diastereotopic. The spectra at 200 MHz display distinct multiplets in the region δ 3–5 due to five inequivalent protons on the η^6-arene ligand; these peaks

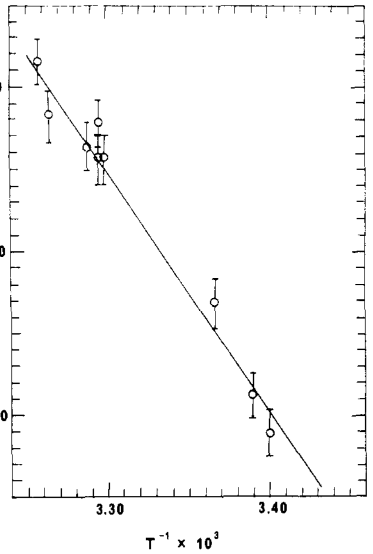

Figure 3. The Arrhenius plot for the reaction of the complex Mo(η^6-PhPMePh)(PMePh$_2$)$_3$ with carbon monoxide in toluene.

were assigned for the spectrum of complexes 2 and 3 (Figure 2) by selective decoupling experiments. Assignment of these peaks for complexes 4 and 5 is not possible because of the presence of peaks in the same spectral region due to complex 1. The large upfield displacement ($\Delta\delta \approx 3.3$ on average) of these arene resonances from their unperturbed values at ~7.1 ppm is a consequence of shielding by the electron-rich molybdenum center. This shift is, as expected, greater than the average shift $\Delta\delta \approx 2.1$ for analogous chromium and molybdenum tricarbonyl π-bonded arylphosphine complexes[7b,d,e] which are less electron rich. Six distinct resonances for ^{13}C nuclei on the η^6-arene ring in complex 3 are found at δ 84–76 or ~50 upfield of uncomplexed phenyl carbons.

IR Spectra. The stretching frequencies of the unsaturated ligands in complexes 3, ν(CN) = 1940, 4, ν(CO) = 1830, and 5, $\nu(N_2)$ = 1980 cm^{-1}, are much lower (~300 cm^{-1}) than free ligand values because they are conjugated to an electron-rich molybdenum center. Other known electron-rich complexes give similar stretches: Mo(dppe)$_2$(CNCMe$_3$)$_2$,[19] ν(CN) = 1915 cm^{-1}; Mo(η^6-C$_6$H$_6$)(CO)(PPh$_3$)$_2$,[2d] ν(CO) = 1808 cm^{-1}; Mo(η^6-C$_6$H$_5$CH$_3$)(N$_2$)(PMePh$_2$)$_2$,[2d] $\nu(N_2)$ = 1970 cm^{-1}. The broad isocyanide vibration of 3 (2000–1800 cm^{-1}) may result from the bent CN(CMe$_3$) group (see below) adopting a variety of conformations in solution.[20]

Gas-Uptake Kinetics. The rates of reaction of complex 1 in toluene with carbon monoxide at pressures of less than 1 atmosphere were studied using a constant pressure gas uptake apparatus (Table II). The rate equation for reaction 3 is first order in the concentration of 1 and zero order in carbon monoxide pressure (runs 4–7):

$$\text{rate} = k_1[1] \quad k_1(303\ \text{K}) = (1.5 \pm 0.1) \times 10^{-3}\ \text{s}^{-1}$$

The Arrhenius plot for the reaction (Figure 3) has a correlation coefficient of 0.990 and yields the activation parameters ΔH^{*} = 28.8 ± 1.6 kcal mol^{-1} and ΔS^{*} = 23 ± 5 cal K^{-1} mol^{-1}. These parameters likely also apply for reactions of 1 with the other small, strongly coordinating ligands; half-life measurements by ^{31}P NMR for the isocyanide reaction under argon[21] gave the expected rate for

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[18] Vincent, E.; Verdonck, L.; van der Kelen, G. P. *Spectrochim. Acta, Part A* **1980**, *36A*, 699.

[19] Chatt, J.; Elson, C. M.; Pombeiro, A. J. L.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1978**, *165*.

[20] Harris, G. W.; Albers, M. O.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1983**, *2*, 609.

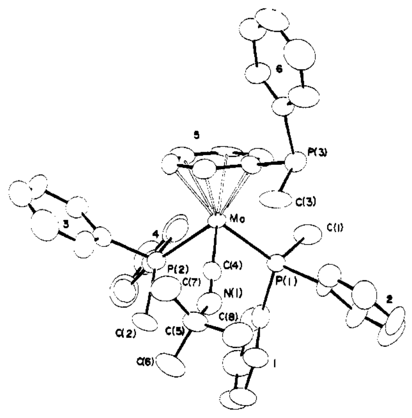

Figure 4. The ORTEP diagram and atom numbering scheme for the molecule Mo(η^6-PhPMePh)(CNCMe$_3$)(PMePh$_2$)$_2$ (**3**).

this first-order reaction at 33 °C (2.3×10^{-3} s^{-1}, run 10).

Thus the mechanism of reaction 3 involves the rate-determining dissociation of a σ-bonded ligand from complex **1** to give the intermediate Mo(η^6-PhPMePh)(PMePh$_2$)$_2$ which is scavenged rapidly by strongly coordinating ligands L:

$$\underset{\mathbf{1}}{\mathrm{Mo}(\eta^6\text{-P})(\mathrm{P})_3} \xrightarrow[-\mathrm{P}]{k_1} \text{“}\mathrm{Mo}(\eta^6\text{-P})(\mathrm{P})_2\text{”} \xrightarrow[+\mathrm{L}]{\text{fast}} \underset{\mathbf{2\text{–}4}}{\mathrm{Mo}(\eta^6\text{-P})(\mathrm{L})(\mathrm{P})_2} \quad (4)$$

Weakly bonding dinitrogen reacts in competition with dissociating phosphine and gives a rate 5 times slower than expected for eq 4.[4] The activation enthalpy observed (29 kcal) matches those found for reactions involving phosphine dissociation from group 6 metal carbonyls (29–32 kcal mol^{-1})[22] and reflects the metal–phosphorus bond strength.

This dissociative mechanism contrasts with the associative mechanism found for substitution reactions of Mo(η^6-arene)(CO)$_3$[23] which involves an intermediate containing an η^4-arene ligand.[24] The latter route would explain the facile conversion of complexes Cr(η^6-ArPAr$_2$)(CO)$_3$ and [Cr(η^6-ArPAr$_2$)(CO)$_2$]$_2$ to Cr(CO)$_5$(PAr$_3$) by reaction with 1 atm of carbon monoxide at 25 °C.[7d] By contrast, only σ-bonded ligands are displaced from **1** by strongly coordinating ligands such as carbon monoxide and 1,2-bis(diphenylphosphino)ethane. Complex **1** reacts differently because of its labile ligands and its strong metal–arene bond. Studies of other group 6 π-arene complexes provide evidence that the replacement of π-acid ligands by electron-donating phosphine ligands strengthens the metal–arene interaction as judged by the increased difficulty in displacing the arene by other ligands.[25]

X-ray Crystallographic Analysis of Mo(η^6-PhPMePh)(CNCMe$_3$)(PMePh$_2$)$_2$. An ORTEP diagram of complex **3** with the atom numbering scheme and a stereoview of the molecule are shown in Figures 4 and 5, respectively. Relevant bond lengths and angles are listed in Table V. The crystal structure consists of monomeric molecules of **3** separated by normal van der Waals distances. The geometry about the molybdenum is distorted octahedral with the σ-bonded PMePh$_2$ and CNCMe$_3$ ligands occupying one face of the octahedron and the η^6-bonded ring, the other face. Two other molybdenum complexes containing η^6-arylphosphine ligands have been the subject of structural studies: Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ (**7**)[3c] and Mo(η^6-(p-tol)P{Mo(CO)$_5$}(p-tol)$_2$)(CO)$_3$ (**8**).[7b]

The geometries of the η^6-bonded ligand in complexes **3** and **7** are very similar. The Mo–C(arene) distances for **3** (2.24 (1)–2.32 (1) Å) average to 2.28 (1) Å as do those of **7**. These short bond lengths suggest a stronger metal–arene interaction than is observed in the Mo(η^6-arene)(CO)$_3$ moiety of compound **8** (average Mo–C(arene) = 2.347 (9) Å); this is consistent with the differences in the substitution chemistry between the phosphine and carbonyl systems as discussed above. Bond lengths for the complexes Mo(η^6-C$_6$H$_6$)(Me)$_2$(PMe$_2$Ph)$_2$ (average Mo–C(arene) = 2.30 (2) Å) and Mo(η^6-C$_6$H$_5$CH$_3$)(Me)$_2$(PMe$_2$Ph)$_2$ (average = 2.30 (1) Å)[5b] are intermediate, but these complexes show ring distortions that would favor η^4 bonding, whereas in **3** and **7** the rings are planar with no obvious alternations in C–C distances. The free phosphorus atom P3 is displaced out of the plane of the ring and away from the molybdenum by 0.265 (3) Å for **3** and 0.32 Å for **7**. It makes no close (<3.6 Å) intra- or intermolecular Mo–P contacts. The η^6-arene in **3** aligns with the tripod of ligands in an almost eclipsed configuration (see Figure 5) with the bonds Mo–C52, Mo–C54, and Mo–C56 approximately eclipsing bonds Mo–P1, Mo–P2, and Mo–C4, respectively. Distortions from an eclipsed geometry cause the PMePh group on the η^6 ring to lie slightly closer to the bond Mo–C4 than to Mo–P1 as judged by the torsion angles C4–Mo–C51–P3 and P1–Mo–C51–P3 of 42.3 and −49.7°, respectively. The CNCMe$_3$ and CO$_2$Me groups in the complex Cr(η^6-C$_6$H$_5$CO$_2$Me)(CNCMe$_3$)(CO)$_2$ are aligned in a similar fashion.[20] The substituents on the free phosphorus are oriented with the methyl on P3 endo to the plane of the ring by 0.57 Å and pointing toward the *tert*-butyl group. The larger phenyl group is exo to the plane presumably to avoid steric interactions. The free phosphorus in complex **7** also has methyl substituents endo and exo to the ring.

The Mo–P distances of 2.416 (3) and 2.420 (3) Å in **3** are short for molybdenum(0) complexes[7b,26] but are comparable in length to two of the bonds in complex **7** (Mo–P = 2.423 (5), 2.434 (4), 2.451 (6) Å; the longest is nearest the PMe$_2$ group on the η^6 ring). An important feature of complex **3** is the large P–Mo–P angle of 94.0 (1)° and small PMoC4 angles of 88.5 (3)° and 83.5 (3)°. The large phosphine ligands have moved away from each other and toward the small isocyanide ligand instead of maintaining a geometry closer to octahedral as is observed for complex **7** with P–Mo–P angles of 89.8 (2)°, 91.6 (2)°, and 93.0 (2)°. Steric interactions between the ligands are evident from the considerable widening of angles MoPC1, MoPC2, MoPC11, MoPC21, and MoPC41 (117.8 (5)–121.2 (4)°) from tetrahedral angles and the deviation of P2 by 0.158 (3) Å out of the plane of ring 3 (Table VIII).

The structural features of the isocyanide ligand in **3** are consistent with a strong Mo–C interaction involving significant π back-bonding from the electron-rich metal. The Mo–C4 distance of 1.984 (13) Å is shorter than ones in the

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(21) If solutions of complex **1** are allowed to equilibrate with nitrogen, then rates 10–20% higher are observed due to the presence of small quantities of complex **5** at the onset of reaction.

(22) (a) Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488. (b) Darensbourg, D. J.; Graves, A. H. *Ibid.* **1979**, *18*, 1257.

(23) Zingales, F.; Chiesa, A.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2707.

(24) (a) Bond, A.; Bottrill, M.; Green, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2372. (b) Salzer, A. *J. Organomet. Chem.* **1976**, *117*, 245. (c) Huttner, G.; Lange, S. *Acta Crystallogr. Sect. B* **1972**, *B28*, 2049.

(25) (a) Semmelhack, M. F.; Seufert, W.; Keller, L. *J. Organomet. Chem.* **1982**, *226*, 183. (b) Choi, H. W.; Sollberger, M. S. *Ibid.* **1983**, *243*, C39.

(26) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L.; Royston, G. H. D.; Muir, K. W.; Walker, R. *J. Chem. Soc., Chem. Commun.* **1975**, 708.

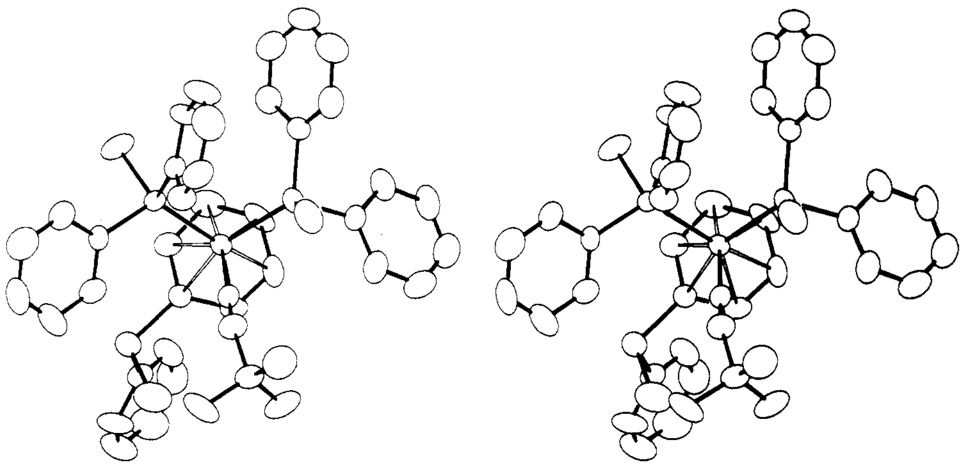
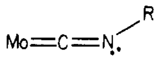


Figure 5. A stereoview of complex 3.

molybdenum(0) complex $Mo(CNMe)_2(PPh_2CH_2CH_2PPh_2)_2$ (2.101 (7) Å) (**9**)[26] and in the molybdenum(II) complexes $Mo(\eta^5\text{-}C_5H_5)(CNPh)(CO)_2I$ (2.025 (10) Å),[27] $Mo(\eta^5\text{-}C_5H_5)(CNCMe_3)(CF_3)(Me_3CNCC(CF_3)C(CF_3)C(CF_3)C(CF_3))$ (2.091 (14) Å),[28] and $Mo\{\eta^3\text{-}CMeCMeCMeC(O)O\}(CNCMe_3)(\eta^5\text{-}C_5H_5)(CO)$ (2.053 (5) Å).[29] The C4–N distance of 1.222 (15) Å is longer than those of the other compounds (1.10 (1), 1.153 (13), 1.158 (21), and 1.153 (7) Å, respectively) and that of free CNMe (1.166 (1) Å)[30] and agrees with the low CN stretch of 1940 cm^{-1} observed for **3**. There is a pronounced bend at the nitrogen of the $CNCMe_3$ ligand (angle C4–N–C5 = 150 (1)°, angle Mo–C4–N = 178 (1)°, and this compares with an angle of 156 (1)° observed for the electron-rich and sterically crowded complex **9**. The C–N–C angles in the three molybdenum(II) complexes are close to 180° (174 (1)°, 177 (2)°, 169.5 (7)° as above). Angles down to 129° have been observed for isocyanides in some low valent complexes[31] and have been attributed more to a steric distortion of bonding mode I than to a rehybridization at nitrogen, mode II.[32] However the electron-rich molybdenum complex **9** can be protonated at nitrogen as expected for valence structure II.[33] The reaction of **3** with HBF_4 in THF yields uncharacterized, oxidized products (ν(CN) = 2070 cm^{-1}) but no products protonated at nitrogen. Electronic factors may cause the CMe_3 group to angle down toward the η^6 ring,[20] but steric factors must be responsible for its sideways displacement toward phenyl ring 3 (Figure 4) which is the ring least affected by steric repulsions (Mo–P2–C31 is only 110.9 (4)° whereas all other Mo–P–C angles are 118–121°).

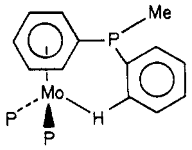
I



II

Summary. The reactions and spectral properties of complex 1 show that it is a very electron-rich complex with bulky, labile σ-bonded ligands. Substitution reactions proceed via a dissociative mechanism for a wide variety of ligands with cone angles less than ~136°. The primary reason for the lability of the phosphine ligands in 1 is a weakening of the molybdenum–phosphorus bonds caused by mutual steric interactions between the bulky *fac*-bonded ligands. For example $Mo(\eta^6\text{-picoline})(PMePh_2)_3$[15] and $FeH_2(PMePh_2)_4$[4] also contain labile *fac*-bonded ligands. The structural analysis of $Mo(\eta^6\text{-PhPMePh})(CNCMe_3)(PMePh_2)_2$ shows that the phosphorus-coordinated ligands minimize steric repulsions by adopting a wide angle P–Mo–P of 94°, 4° larger than expected for an octahedral coordination geometry.

The phosphorus substituent on the arene ring can also contribute to the weakening of σ bonds in 1. In crystals of 3 it is situated close to the smaller isocyanide ligand possibly to avoid steric interactions with the larger phosphine ligands, an unavoidable situation in complex 1. This dangling substituent may also play a role in stabilizing the $Mo(\eta^6\text{-PhPMePh})(PMePh_2)_2$ intermediate (eq 4) by way of an ortho phenyl hydrogen interaction with the coordinatively unsaturated molybdenum center (III). A variety of such M-H-C interactions have recently been observed.[34]



III

Complex 1 undergoes a variety of oxidative addition reactions that are currently being investigated; a reaction with hydrogen has been reported.[4] Preliminary results indicate that it is not a catalyst for the hydrogenation of 1-hexene.

The concept of a σ to η^6 bonding rearrangement of an arylphosphine ligand accounts for the formation of complex 1 in such high yield and has been applied to the syntheses of other new molybdenum complexes containing η^6-bonded ligands.[7a,15,35]

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[27] Sim, G. A.; Sime, J. G.; Woodhouse, D. I.; Knox, G. R. *Acta Crystallogr., Sect. B* **1979**, *B25*, 2406.

[28] Davidson, J. L.; Green, M.; Nyathi, J. Z.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2246.

[29] Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1067.

[30] Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 3021.

[31] Bassett, J.-M.; Berry, D. E.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1003.

[32] Carroll, W. E.; Green, M.; Galas, A. M. R.; Murray, M.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 80.

[33] Chatt, J.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1980**, 492.

[34] Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649.

[35] Luck, R.; Morris, R. H.; Sawyer, J., in press.

Organometallics 1984, *3*, 255–263

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Registry No. 1, 84430-77-3; 2, 84430-78-4; 3, 87902-57-6; 4, 87902-58-7; 5, 87902-59-8; Mo(η^6-PhPMePh)(NCMe)($PMePh_2$)$_2$, 87902-60-1; Mo(η^6-PhPMePh)(PMe_3)($PMePh_2$)$_2$, 87902-61-2; Mo(η^6-PhPMePh)(PMe_2Ph)($PMePh_2$)$_2$, 87902-62-3; Mo(η^6-PhPMePh)$(CO)_2$($PMePh_2$), 87902-63-4; molybdenum pentachloride, 10241-05-1; acetylene, 74-86-2.

Supplementary Material Available: Tables VI–X containing bond lengths and bond angles for the phenyl rings, thermal parameters, least-squares mean planes, root-mean-square vibration amplitudes, and final structure amplitudes (23 pages). Ordering information is given on any current masthead page.

Group 4A 9,10-Dihydro-9,10-diheteroanthracenes: Synthesis and Structure

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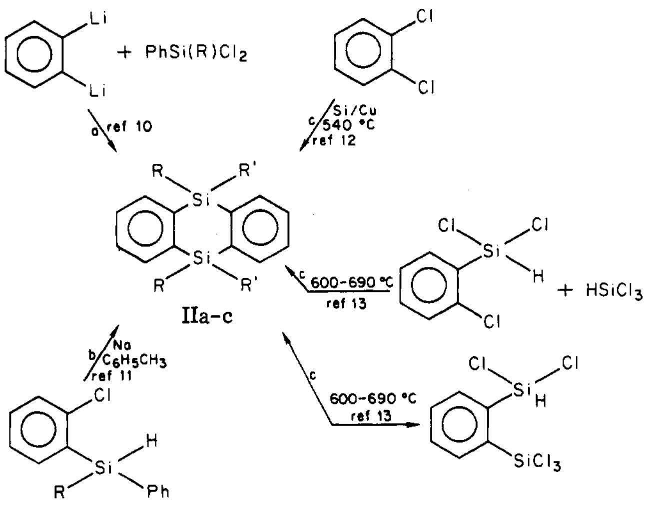
9,10-Dihydro-9,10-diheteroanthracenes are prepared by a ring closure reaction of a dilithio or di-Grignard intermediate prepared from (o-XC_6H_4)$_2$SiMeR (R = H, Me; X = Cl, Br) with $RR'MCl_2$ (R or R′ = H, Me, Ph; M = Si, Ge, Sn, Pb). Compounds that contain a silicon atom with germanium, tin, or lead are a previously unreported class of compounds. The molecular structures of 9,9,10,10-tetramethyl-9,10-dihydro-10-germa-9-silaanthracene, IIIa, and 9,9,10,10-tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene, IIIb, have been determined by X-ray diffraction methods. The crystal data are as follows: compound IIIa, orthorhombic, *Pbca*, a = 9.585 (5) Å, b = 16.200 (12) Å, c = 21.236 (12) Å, Z = 8, 1512 observed data yielded a final R value of 0.043 by least-squares refinement (of a model with disordered silicon and germanium atoms); compound IIIb, monoclinic, $P2_1/n$, a = 18.897 (8) Å, b = 9.093 (6) Å, c = 19.439 (13) Å, β = 95.60°, Z = 8, 3475 observed data yielded a final R value of 0.051 for least-squares refinement. Molecules of compounds IIIa and IIIb exist in a "butterfly" shape with a boat conformation in the central 6-membered diheterocyclic ring. The dihedral angles of the benzo groups in compounds are 153° (IIIa) and 142° and 148° for the two independent molecules of IIIb. This boat conformation gives rise to pseudoaxial and pseudoequatorial geminal methyl groups that are equivalent as determined by both ^1H and ^{13}C NMR between room temperature and −95 °C.

Introduction

Dihydroanthracenes that contain group 4A heteroatoms (Si, Ge, Sn) were reported in the early 1970s.[1] An example, dihydrosilaanthracene, I, is illustrated in Figure 1. In the parent class of diheteroanthracenes, II, the only derivatives that contain group 4 heteroatoms in both 9- and 10-positions are those where X = Y = Si[2] and Ge,[3] although the tin derivative has been mentioned with no details.[4] Derivatives where all aromatic hydrogens in II have been replaced by fluorine have also been reported for Si,[5] Ge,[6] and Sn.[7] No diheteroanthracenes of type III have been previously reported. Dihydrosilaanthracenes, I, have been prepared by a route developed by Jutzi[1] and modified by Corey.[8] Bis(o-chlorophenyl)methane, IV, prepared in a multistep sequence, is the precursor to the di-Grignard intermediate used in the ring closure reaction with dichlorosilanes. Another study concluded that IV and not the corresponding bromo and iodo derivative was the precursor of choice to dihydrosilaanthracenes in spite of the difficulty in forming Grignard reagents from aryl chlorides.[9]

Scheme I



IIa, R = R′ = Ph; IIb, R = Ph, R′ = Ph, n-$C_{12}H_{25}$, CH_3; IIc, R = R′ = Cl

Two general routes to diheteroanthracenes have been developed. Gilman and co-workers produced the first disilaanthracene (DSA), II (X = Y = Si), by a coupling reaction of ortho-substituted aromatic derivatives in the presence of sodium or lithium[10,11] (Scheme I). This ap-

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[1] Jutzi, P. *Chem. Ber.* **1971**, *104*, 1455.

[2] Barton, T. J. "Comprehensive Organometallic Chemistry"; 1st Ed., Pergamon Press, Elmsford, NY, 1982; Vol. 2, p 273.

[3] D'yachenko, O. A.; Soboleva, S. V.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1976**, 496.

[4] Dereu, N. L. M.; Zingaro, R. A. *J. Organomet. Chem.* **1981**, *212*, 141.

[5] Haiduc, I.; Gilman, H. *J. Organomet. Chem.* **1968**, *11*, 55.

[6] Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1968**, *12*, 341.

[7] Lanthier, G. F.; Miller, J. M.; Cohen, S. C.; Massey, A. G. *Org. Mass Spectrom.* **1974**, 235. No synthetic details of this single example have been published.

[8] Corey, J. Y.; Dye, M. J.; Farrell, R. L.; Mitchell, M. V. *J. Organomet. Chem.* **1978**, *153*, 127.

[9] Bickelhaupt, F.; Jongsma, C.; de Koe, P.; Lourens, R.; Mast, N. R.; van Mourk, G. L.; Vermeer, H.; Weustink, R. J. M. *Tetrahedron* **1976**, 1921.

[10] Gilman, H.; Zeuch, E. A. *J. Am. Chem. Soc.* **1960**, *82*, 3605.

[11] Gilman, H.; Zeuch, E. A.; Steudel, W. *J. Org. Chem.* **1962**, *27*, 1836.

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