Notes

Complexes containing Mercury–Molybdenum Bonds: New Compounds of the Type $[HgX\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ (L = arsine or phosphine). Crystal and Molecular Structure of the Complex $[Hg(CN)\{trans\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$ ‡

Geoffrey Salem, Brian W. Skelton, Allan H. White,* and Stanley Bruce Wild †
Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, Western Australia 6009

The series of Hg–Mo bonded complexes $[Hg(CN)\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ (where L = $AsMe_2Ph$, PMe_2Ph, $PMePh_2$, or PPh_3) have been prepared from $Hg(CN)_2$ and the salts $Na[Mo(CO)_2L(\eta^5\text{-}C_5H_5)]$ or dimers $[Hg\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}_2]$. The cyanomercury complexes are extremely useful intermediates for the facile synthesis of the derivatives $[HgX\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ (where X = Cl, Br, I, NO_3, O_2CMe, OCN, SCN, or S_2CNEt_2). The molecular structure of the complex $[Hg(CN)\{trans\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$ has been determined by single-crystal *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with a = 14.570(4), b = 12.457(3), c = 10.783(3) Å, β = 114.04(2)°, and Z = 4. The structure was solved by heavy-atom methods and refined by least squares to a residual of 0.037 for 2 218 reflections with $|I_o| > 3\sigma(I)$. The Hg–Mo bond length [2.654(1) Å] is the shortest hitherto observed.

In an article concerning mercury derivatives of tertiary phosphine substituted carbonyl anions of manganese(−I), Hieber *et. al.* [1] described the compound $[\{HgMn(CO)_3(PPh_3)_2\}_2]$. The dimer was light-sensitive and apparently contained the Mn–Hg–Hg–Mn bonding arrangement. It was produced in a redox reaction involving the substituted metal carbonyl anion and mercury(II) cyanide. In an attempt to prepare similar compounds of molybdenum, we have investigated the reactions of $Na[Mo(CO)_2L(\eta^5\text{-}C_5H_5)]$ (where L = $AsMe_2Ph$, PMe_2Ph, $PMePh_2$, or PPh_3) with $Hg(CN)_2$. However, depending upon the reaction conditions, either $[Hg(CN)\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ or $[Hg\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}_2]$ were isolated. The former proved to be extremely attractive precursors to the variety of compounds $[HgX\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ (where X = Cl, Br, I, NO_3, O_2CMe, OCN, SCN, or S_2CNEt_2), due to the ready displacement of the cyanide group. Nevertheless, the Co–Hg–Hg–Co bonding arrangement has recently been confirmed in the compound $[\{HgCo[N(CH_2CH_2PPh_2)_3]\}_2]$.[2]

Results and Discussion

The Complexes $[Hg\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}_2]$.—These were prepared from $[Hg\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ and the appropriate ligand by heating in a medium-to-high boiling solvent. The triphenylphosphine-substituted compound was prepared in ethanol as previously described,[3] but using a longer reaction time (6 h). Boiling light petroleum (b.p. 100—120 °C) however was found to be a better medium for the synthesis of the PMe_2Ph and $PMePh_2$ derivatives, yields of *ca.* 90% being obtained after reaction times of 2 and 10 h, respectively. The complex containing $AsMe_2Ph$ was produced in 76% yield in di-n-butyl ether after 45 h at 140 °C. The substituted dimers (Table 1) are air-stable crystalline solids, which are convenient precursors to halide-free solutions of the corresponding substituted metal carbonyl anions (Scheme). According to spectroscopic measurements (Table 1) the dimers have structures based upon a linear mercury geometry involving *trans*-substituted pseudo-square-pyramidal molybdenum atoms. It is noteworthy that the thermal substitution of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ by tertiary arsines invariably led to *cis*-substituted products,[4] whereas tertiary phosphines produced mixtures of the two possible geometric isomers.[5]

Reduction of the substituted dimers with *ca.* 1% sodium amalgam afforded solutions of the respective substituted metal carbonyl anion. The alternative method of producing anions of this type, involving sodium amalgam reduction of *cis*- or *trans*-$[Mo(CO)_2L(\eta^5\text{-}C_5H_5)I]$, is unsatisfactory if cyanomercury complexes are to be isolated directly from the reaction mixture, since the iodide ions readily displace the cyano-group (see below).

The Complexes $[Hg(CN)\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$.—Reaction of halide-free solutions of the salts $Na[Mo(CO)_2L(\eta^5\text{-}C_5H_5)]$ (where L = $AsMe_2Ph$, PMe_2Ph, $PMePh_2$, or PPh_3) with one equivalent of $Hg(CN)_2$ produced the light-sensitive, but air-stable, crystalline solids $[Hg(CN)\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$ in high yield (Scheme). Ligand-exchange reactions between the symmetrical mercurials $[Hg\{trans\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}_2]$ and $Hg(CN)_2$ also led to the unsymmetrical cyanomercury compounds (Table 1). The ν(HgCN) vibration in the various complexes was observed as a weak absorption in the region 2 010—2 145 cm^{-1}. The dimethylphenylarsine and triphenylphosphine derivatives are monomeric in dichloromethane solution as determined by the method of isothermal distillation. The *trans* geometry of the complexes containing $AsMe_2Ph$ or a tertiary phosphine ligand was confirmed by ^1H n.m.r. spectroscopy. A sharp singlet was

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* For correspondence on crystallography.

† For correspondence on chemistry. *Present address:* Research School of Chemistry, The Australian National University, Canberra, A.C.T. 2600, Australia.

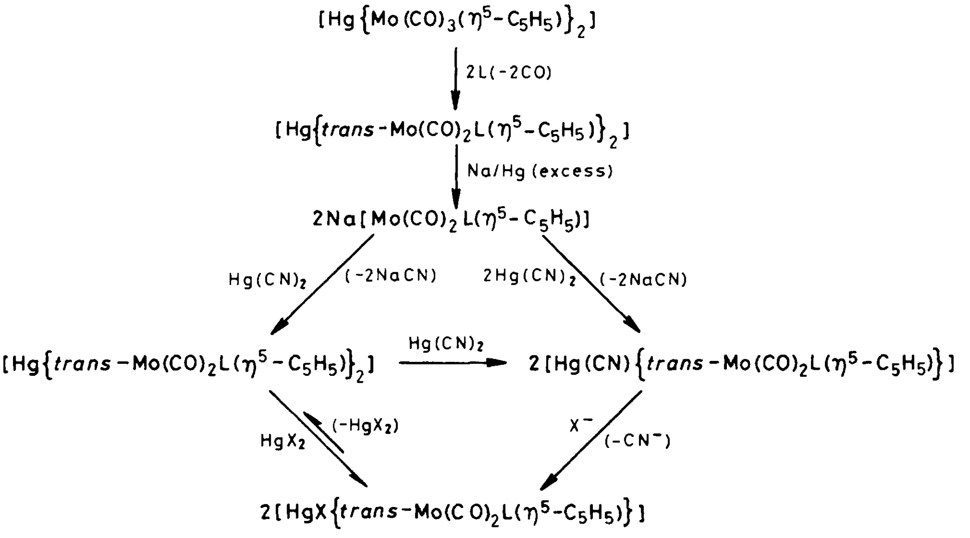
‡ Dicarbonyl(cyanomercurio)(η-cyclopentadienyl)(dimethylphenylarsine)molybdenum.

Supplementary data available (No. SUP 23651, 14 pp.): thermal parameters, H-atom co-ordinates, least-squares planes, ring geometries, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical data and selected spectroscopic properties of the complexes $[Hg\{\textit{trans}\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}_2]$ and $[HgX\{\textit{trans}\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$

Complex	M.p. (decomp.) (°C)	Analysis[a] (%)		$\nu(CO)$[b]/cm^{-1}	^{1}H N.m.r. spectra[c]	
		C	H		δ(EMe)	$\delta(\eta^5\text{-}C_5H_5)$
$[Hg\{\textit{trans}\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}_2]$	160	36.2 (36.1)	3.3 (3.2)	1 885s, 1 856s, 1 807vs	1.71s	5.12s
$[Hg\{\textit{trans}\text{-}Mo(CO)_2(PMe_2Ph)(\eta^5\text{-}C_5H_5)\}_2]$	159	40.0 (39.6)	3.5 (3.5)	1 882s, 1 853s, 1 804vs	1.87d[d]	4.87br,s
$[Hg\{\textit{trans}\text{-}Mo(CO)_2(PMePh_2)(\eta^5\text{-}C_5H_5)\}_2]$	196	46.6 (46.4)	3.5 (3.5)	1 880s, 1 859s, 1 809vs	2.11d[d]	4.90br,s
$[Hg\{\textit{trans}\text{-}Mo(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)\}_2]$[e]				1 892s, 1 865s, 1 816vs		4.97br,s
$[Hg(CN)\{\textit{trans}\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$	155	30.9 (30.7)	2.6 (2.6)	1 916s, 1 843vs	1.79s	5.09s
$[Hg(CN)\{\textit{trans}\text{-}Mo(CO)_2(PMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$	176	33.3 (33.0)	3.0 (2.8)	1 913s, 1 839vs	1.88d[d]	4.88br,s
$[Hg(CN)\{\textit{trans}\text{-}Mo(CO)_2(PMePh_2)(\eta^5\text{-}C_5H_5)\}]$	158	39.3 (39.1)	2.7 (2.8)	1 914s, 1 842vs	2.12d[d]	4.91br,s
$[Hg(CN)\{\textit{trans}\text{-}Mo(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)\}]$	196	44.0 (44.2)	2.8 (2.9)	1 921s, 1 851vs		4.89br,s
$[Hg(NO_3)\{\textit{trans}\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$	125	27.4 (27.2)	2.6 (2.4)	1 940s, 1 865vs	1.77s	5.04s
$[Hg(NO_3)\{\textit{trans}\text{-}Mo(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)\}]$	140	40.6 (40.5)	2.9 (2.7)	1 945s, 1 869vs		5.08br,s

[a] Calculated values in parentheses. [b] Recorded in CH_2Cl_2. [c] Chemical shift values in p.p.m. relative to $SiMe_4$; in $CDCl_3$. [d] $J = 8$ Hz. [e] Ref. 9.



Scheme.

observed for the AsMe groups in the tertiary arsine derivative. In *cis* compounds of this type the molybdenum atom is asymmetric and a pair of singlets for the diastereotopic AsMe groups is observed.[4] Similarly, a doublet ($J = 8$ Hz) was observed for the equivalent PMe groups in the PMe_2Ph derivative. The broadness of the cyclopentadienyl resonance in all of the tertiary phosphine-containing complexes was also an indication of the *trans* geometry. In *cis* complexes ^{31}P coupling to the cyclopentadienyl protons is negligible.[5] Furthermore, the ratio of the intensities of the $\nu(CO)$ absorptions in all of the complexes was consistent with the *trans* formulation.[6]

Crystal and Molecular Structure of $[Hg(CN)\{\textit{trans}\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)\}]$.—In the solid state, the molybdenum atom in this complex has a pseudo-square-pyramidal stereochemistry. The cyanomercury and tertiary arsine moieties are situated *trans* to each other at the base of the pyramid (Figure). The Mo–Hg bond length [2.654(1) Å, Table 2] is shorter than that found in the compound $[HgI\{\textit{trans}\text{-}Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}MeC_5H_4)\}]$ [2.685(3) Å].[7] The Mo–Hg–CN arrangement is almost linear (Table 3). Compared to $Hg(CN)_2$, where the lengths of the Hg–C bonds are 2.015 Å and the C–N bonds 1.137 Å,[8] the corresponding bond lengths in the molybdenum complex are longer [2.10(1) Å] and similar [1.13(2) Å], respectively.

The Complexes $[HgX\{\textit{trans}\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$.—The cyanomercury complexes can be converted into a wide range of compounds of the type $[HgX\{\textit{trans}\text{-}Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$. Metathesis with sodium halides gave the halogeno-derivatives (X = Cl, Br, or I) and with sodium diethyldithiocarbamate the corresponding dithiocarbamato-complexes ($X = S_2CNEt_2$) in *ca.* 90% yield. These derivatives are much less light-sensitive than the cyano-compounds. Ligand exchange between the appropriate symmetrical mercurials produced the same complexes.[9] The i.r. spectra of the diethyldithiocarbamato-complexes agree closely with those of certain mono-substituted metal carbonyl derivatives, where the dithiocarbamate ligand is behaving as a chelating agent.[10]

We have also isolated nitratomercury derivatives where $L = AsMe_2Ph$ or PPh_3 (Table 1). They were obtained in almost quantitative yield from the respective cyanomercury complexes by reaction with silver nitrate, or by the exchange reaction between the symmetrical mercurial and $Hg(NO_3)_2$. The nitratomercury complexes are non-electrolytes in dichloromethane solution and each exhibits $\nu(NO_3)$ absorptions at *ca.* 1 425 and 1 310 cm^{-1}, which is typical of the nitrato-group

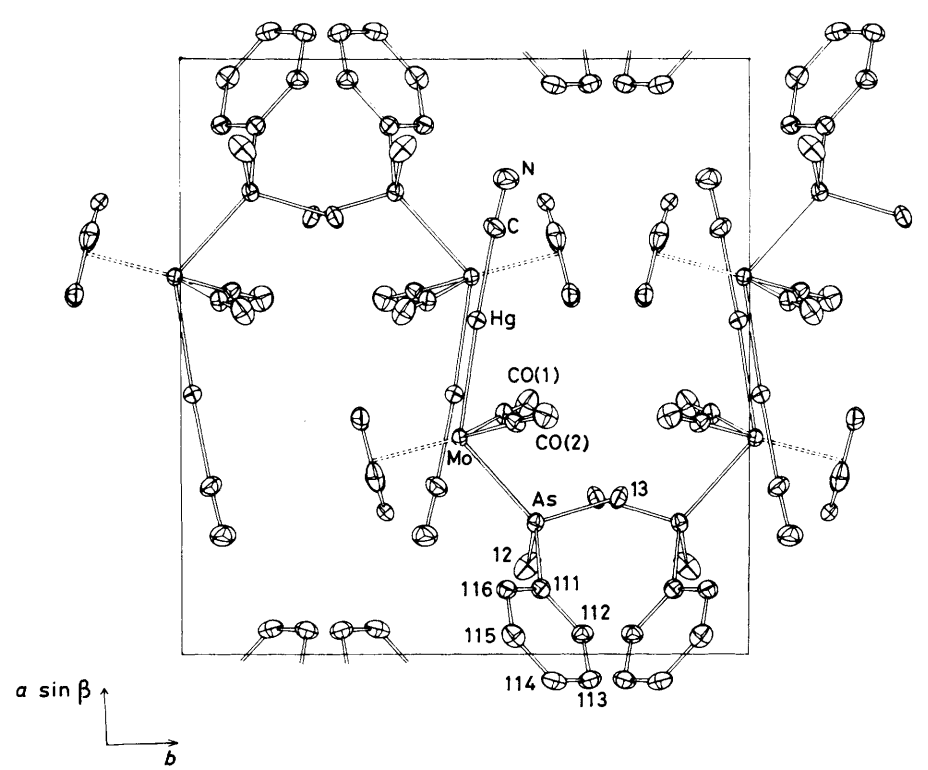


Figure. Unit-cell contents projected down *c* showing the non-hydrogen atom labelling (20% thermal ellipsoids)

Table 2. Interatomic distances (Å) with estimated standard deviations (e.s.d.s) * in parentheses

Mo–C(21)	2.37(1)	As–C(12)	1.95(2)	Hg–C	2.10(1)	Mo–C(1)	1.96(1)
Mo–C(22)	2.35(1)	As–C(13)	1.92(1)	C–N	1.13(2)	C(1)–O(1)	1.16(1)
Mo–C(23)	2.31(1)	As–C(111)	1.96(1)	Hg–Mo	2.654(1)	Mo–C(2)	1.96(1)
Mo–C(24)	2.33(1)	C(2*m*)–C(2*n*)	1.36(2)—1.44(2)	Mo–As	2.539(1)	C(2)–O(2)	1.16(1)
Mo–C(25)	2.33(1)	C(11*m*)–C(11*n*)	1.38(2)—1.39(2)				

* Right adjusted to the least significant figure of the preceding number.

Table 3. Interatomic angles (°) with e.s.d.s in parentheses

C–Hg–Mo	177.3(4)	Hg–Mo–As	130.57(4)	C(12)–As–C(13)	102.6(6)
Hg–C–N	176(1)	As–Mo–C(1)	79.6(3)	C(12)–As–C(111)	100.9(5)
Hg–Mo–C(1)	72.3(3)	As–Mo–C(2)	77.1(3)	C(13)–As–C(111)	99.8(4)
Hg–Mo–C(2)	72.9(3)	C(1)–Mo–C(2)	106.0(4)	As–C(111)–C(112)	118.9(8)
Hg–Mo–C(21)	116.3(4)	Mo–C(1)–O(1)	175.8(8)	As–C(111)–C(116)	121.2(7)
Hg–Mo–C(22)	86.3(3)	Mo–C(2)–O(2)	174.0(11)	C(21)–C(2*m*)–C(2*n*)	107(1)—109(1)
Hg–Mo–C(23)	89.1(4)	Mo–As–C(12)	115.0(4)	C(2*m*)–Mo–C(2*n*)	34.0(4)—36.1(5)
Hg–Mo–C(24)	121.8(3)	Mo–As–C(13)	114.1(4)	C(11*l*)–C(11*m*)–C(11*n*)	119(1)—121(1)
Hg–Mo–C(25)	143.5(3)	Mo–As–C(111)	121.6(3)		

functioning as a unidentate ligand.[11] They are very light-sensitive compounds and even more prone to substitution than the corresponding cyanomercury complexes. For example, the nitrato-group was readily displaced by O_2CMe^-, OCN^-, or SCN^-. The acetatomercury derivatives displayed a sharp singlet in their ^1H n.m.r. spectra at *ca.* δ 1.98 due to the O_2CMe^- group. The i.r. spectra of the complexes are similar to those reported for other metal acetates,[12] although it was not possible to make a definite structural assignment. The cyanato-complexes have i.r. spectra consistent with the usual *N*-bonding. The asymmetric ν(NCO) vibration was observed at 2 167—2 168 cm^{-1} in both complexes and the corresponding symmetric vibration at 1 428—1 432 cm^{-1}. The thiocyanato-derivatives appeared to contain terminal *S*-bonded thiocyanate.[13] In the compound containing dimethylphenylarsine, ν(CN), ν(CS), and ν(HgS) were observed. However, in the corresponding triphenylphosphine-containing complex ν(CS) was obscured by P–C absorptions.

Experimental

Proton n.m.r. spectra were recorded on a Hitachi–Perkin-Elmer R24B spectrometer, i.r. spectra on a Perkin-Elmer model 283 spectrophotometer. The compounds *cis*-$[Mo(CO)_2(AsMe_2Ph)(\eta^5\text{-}C_5H_5)I]$,[4] $[Hg\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$,[14] $[Hg(S_2CNEt_2)_2]$,[15] and [Hg{*trans*-$Mo(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)\}_2]$[3] were prepared by literature methods.

Preparations.—[Hg(CN){*trans*-$Mo(CO)_2L(\eta^5\text{-}C_5H_5)\}]$. A solution of $Na[Mo(CO)_2L(\eta^5\text{-}C_5H_5)]$ in tetrahydrofuran

Table 4. Final atomic co-ordinates

Atom	*x*	*y*	*z*
N	0.799 1(8)	0.572 3(9)	0.367 5(11)
C	0.716 8(9)	0.551 5(9)	0.335 0(11)
Hg	0.562 16(3)	0.520 12(3)	0.264 34(4)
Mo	0.365 11(6)	0.489 64(6)	0.170 15(8)
C(1)	0.390 6(8)	0.587 3(8)	0.045 1(10)
O(1)	0.401 9(6)	0.640 9(7)	−0.035 3(8)
C(2)	0.405 4(8)	0.567 6(7)	0.341 9(10)
O(2)	0.423 0(7)	0.608 5(6)	0.446 0(7)
C(21)	0.300 1(11)	0.340 1(8)	0.024 1(12)
C(22)	0.397 2(10)	0.314 0(8)	0.118 8(14)
C(23)	0.394 4(9)	0.315 8(8)	0.251 1(12)
C(24)	0.296 6(11)	0.340 7(8)	0.232 8(13)
C(25)	0.240 3(8)	0.358 5(7)	0.098 1(12)
As	0.222 85(8)	0.622 99(7)	0.121 36(10)
C(12)	0.149 8(10)	0.609 3(10)	0.236 7(12)
C(13)	0.265 2(8)	0.770 4(8)	0.147 1(12)
C(111)	0.111 6(8)	0.633 1(7)	−0.058 1(10)
C(112)	0.035 4(8)	0.706 3(8)	−0.077 7(10)
C(113)	−0.041 9(8)	0.719 5(9)	−0.204 9(12)
C(114)	−0.043 9(8)	0.656 1(10)	−0.310 7(11)
C(115)	0.032 2(9)	0.584 2(9)	−0.293 7(11)
C(116)	0.110 4(8)	0.572 4(8)	−0.165 8(10)

(thf) was prepared from the corresponding dimer and an excess of *ca.* 1% sodium amalgam by shaking the mixture for 5 min. The amalgam was then separated and the anion treated with $Hg(CN)_2$. Water precipitated the crude products, which were extracted into dichloromethane and purified by recrystallization from dichloromethane–n-hexane. Yields were greater than 90%. Ligand exchange of the corresponding symmetrical mercurials in thf produced identical complexes quantitatively.

[$Hg(NO_3)${*trans*-$Mo(CO)_2L(\eta^5-C_5H_5)$}]. A solution of the corresponding cyanomercury complex in dichloromethane was treated with aqueous $AgNO_3$, the AgCN separated, and the two layers separated. The nitrato-complexes were isolated from the organic component and recrystallized from acetone–diethyl ether (95% yield). Ligand exchange between the symmetrical mercurials gave identical compounds.

[HgX{*trans*-$Mo(CO)_2L(\eta^5-C_5H_5)$}]. These were prepared from the corresponding cyano- or nitrato-complexes in thf by the addition of an excess of the appropriate anion. They were precipitated from the reaction mixture by adding water and then extracted into dichloromethane from which they crystallized in *ca.* 90% yield upon the addition of diethyl ether.

Crystal Structure Determination of [Hg(CN){*trans*-Mo-$(CO)_2(AsMe_2Ph)(\eta^5-C_5H_5)$}].—*Crystal data.* $C_{16}H_{16}AsHgMoNO_2$, M_r = 625.8, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 14.570(4), b = 12.457(3), c = 10.783(3) Å, β = 114.04(2)°, U = 1 787.3(8) Å^3, Z = 4, D_c = 2.33 g cm^{-3}, $F(000)$ = 1 160, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 107 cm^{-1}, 295(1) K. Specimen size: 0.25 × 0.03 × 0.37 mm.

Data collection and refinement. A unique data set was measured within the limit $2\theta < 50°$ at 295(1) K by use of a Syntex $P2_1$ four-circle diffractometer in the conventional 2θ—θ mode. 3 169 Independent reflections were measured, 2 218 with $I > 3\sigma(I)$ being considered ' observed ' and used in the solution and refinement after analytical absorption correction. Refinement was by full-matrix least squares; non-hydrogen atom thermal parameters were refined anisotropically. Hydrogen-atom positional parameters were constrained at estimated trigonal positions with U_H constrained at 1.25 $\bar{U}_{ii}$. Final residuals (R,R',S) were 0.037, 0.042, and 1.2, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Computation was carried out by use of the *X*-RAY 76 program system [16] on a Perkin-Elmer 8/32 computer. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[17] The final atomic co-ordinates are listed in Table 4 and the atom numbering system is shown in the Figure.

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