sulfur compounds is shown in Figure 2.

Two important conclusions can be drawn on the basis of the above results. First, the XPS data for S_2N_2 and S_4N_4 are best interpreted without invoking $N(p\pi)\rightarrow S(d\pi)$ back-bonding. Second, the greater $S\rightarrow N$ charge transfer in S_4N_4 arises from a significant contribution (20%) of valence bond structure IV in which sulfur–sulfur bonds are present. Thus, the XPS data are indicative of a modest S–S bonding interaction, consistent with the S–S distance in the S_4N_4 structure and in accord with a recent UV photoelectron spectroscopic study.[4c]

For comparison we have also calculated atomic charges for S_2N_2 and S_4N_4 by the parameterized MNDO molecular orbital method. The $S\rightarrow N$ charge transfer according to this method is 0.402 e for S_2N_2 and 0.53 e for S_4N_4.[17] The charge transferred calculated by the MNDO MO method is compared with those calculated by other molecular orbital methods in Table III. In agreement with the CHELEQ analysis of the XPS results, all of the methods predict greater $S\rightarrow N$ charge transfer in S_4N_4 than in S_2N_2.

Summary

XPS results, interpreted with the aid of the CHELEQ procedure, show that $N(p\pi)\rightarrow S(d\pi)$ back-bonding is not necessary for a clear understanding of the bonding and charge distribution in S_2N_2 or its precursor S_4N_4. Semiempirical MNDO MO calculations are in agreement with this view. XPS also shows $S\rightarrow N$ charge transfer to be greater in S_4N_4 than in S_2N_2.

Acknowledgment. P.B. would like to thank the National Research Council for the award of a postdoctoral fellowship.

Registry No. S_2N_2, 25474-92-4; S_4N_4, 28950-34-7.

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(17) The minimum energy geometry for S_2N_2 obtained from the MNDO calculations is essentially square with S–N bond lengths of 1.621 Å (1.62 Å experimental) and SNS and NSN angles of 95.0° (92.0° experimental) and 85.0° (88.0° experimental), respectively. The minimum energy geometry of S_4N_4 is largely the same as that which has been experimentally determined except that the MNDO S–S distances are 0.50 Å greater than those reported in the X-ray crystal structure determination. Detailed results of the MNDO calculations will be published elsewhere.

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Synthesis and Molecular Geometry of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

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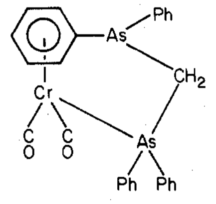
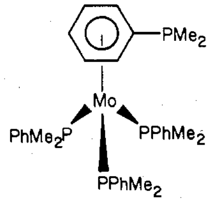
The preparation and structural chemistry of η^6-arene complexes have been investigated thoroughly; in particular, definitive structural studies of $(\eta^6\text{-}C_6H_6)_2Cr$[1] and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$[2] have appeared. A number of complexes have been reported in which a (η^6-arene)→metal linkage arises by interaction of the phenyl (or substituted phenyl) ring of (inter alia) an arylphosphine or an arylarsine ligand with the metal atom. Another unexpected class of molecules thus obtained consists of $[(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]Ru[P(OMe)_3]_2$[3] and related $[(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$Ru-containing complexes.[4]

The ligand $Ph_2AsCH_2AsPh_2$ reacts with $Cr(CO)_6$ in decane yielding the chelate complex I, the crystal structure of which has been reported.[5]



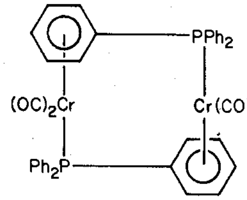
I

A rather less direct route has led to the production of $(PPhMe_2)_4Mo$ which has been shown[6] to have structure II. This appears to be the only nonchelating monomeric complex based upon an η^6-arylphosphine or -arsine to be characterized structurally to date.



II

The reaction of $Cr(CO)_6$ with various triarylphosphine ligands (L) at high temperature has been shown[7] to give rise to two series of complexes of stoichiometry $[Cr(CO)_2L]_2$ and $Cr(CO)_3L$. A structural study of the dimeric species $\{[(\eta^6\text{-}C_6H_5)P(C_6H_5)_2]Cr(CO)_2\}_2$ has revealed[8] the configuration III.



III (schematic, only)

We now report the preparation of a $Cr(CO)_3L$ derivative (L = triphenylarsine), its crystallographic characterization as $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$, and its reaction with $(NMe_3)Cr(CO)_5$.

Experimental Section

Preparation of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$. A mixture of $Cr(CO)_6$ (1.0 g) and $As(C_6H_5)_3$ (3.0 g) in decane (50 mL) was refluxed under argon for 8 h. The resulting orange solution was concentrated and passed down a Florisil column with hexane as eluant. The yellow band was collected, reduced in volume, and cooled to −20 °C overnight, yielding 0.5 g of yellow crystals of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ (25% yield), which were washed with pentane and dried in vacuo; mp 119–120 °C. IR(hexane): ν(CO) 1978 (s), 1914 (s) cm^{-1}. ^1H NMR (CCl_4): δ 7.3 (H, aryl), 5.1–5.0 (H, π-arene); ratio 2:1. Anal.

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Table I. Experimental Data for the X-ray Diffraction Study of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

(A) Crystal Parameters[a] at 24 °C

cryst system: triclinic space group: $P\bar{1}$ [C_i^1; No. 2]
$a = 7.0999$ (8) Å $\alpha = 103.891$ (9)°
$b = 10.5002$ (12) Å $\beta = 101.468$ (8)°
$c = 14.1679$ (13) Å $\gamma = 102.930$ (9)°
$V = 963.1$ (2) Å mol wt = 442.3
$Z = 2$ ρ(calcd) = 1.53 g cm^{-3}

(B) Measurement of Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα (λ = 0.710 730 Å)
monochromator: highly oriented graphite, equatorial mode
reflctns measd: $+h,\pm k,\pm l$
2θ range, deg: 3.5–45.0
scan type: θ(crystal)–2θ(counter)
scan range, deg: $[2.0 + \Delta(\text{Mo K}(\alpha_2 - \alpha_1))]$
scan speed, deg/min: 2.5
reflctns collected: 2921 yielding 2676 independent
std: 070, 008, and $5\bar{2}0$ measured every 97 reflections; no significant changes observed
abs coeff: μ = 24.4 cm^{-1}
abs corr: empirical, by a series of ψ scans[b]
weighting scheme used: $w = [(\sigma|F_o|)^2 + (0.02|F_o|)^2]^{-1}$

[a] Unit-cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of 25 reflections with 26° < 2θ < 35°. [b] For a description of empirical absorption correction see: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* 1977, *16*, 2655.

Table II. Final Positional Parameters, with Esd's[a]

atom	x	y	z
Cr	0.06894 (7)	0.21827 (4)	0.35499 (3)
As	−0.23195 (5)	−0.08340 (3)	0.13467 (2)
C(1)	0.1686 (5)	0.3949 (4)	0.4386 (3)
O(1)	0.2295 (4)	0.5062 (3)	0.4909 (2)
C(2)	−0.0799 (5)	0.1804 (3)	0.4425 (3)
O(2)	−0.1722 (4)	0.1570 (3)	0.4977 (2)
C(3)	−0.1366 (5)	0.2681 (4)	0.2874 (3)
O(3)	−0.2629 (4)	0.3012 (3)	0.2438 (2)
C(11)	−0.3312 (4)	−0.1937 (3)	0.2167 (2)
C(12)	−0.2593 (5)	−0.2995 (3)	0.2366 (3)
C(13)	−0.3330 (7)	−0.3697 (4)	0.2984 (3)
C(14)	−0.4814 (7)	−0.3353 (5)	0.3397 (3)
C(15)	−0.5523 (6)	−0.2320 (5)	0.3211 (3)
C(16)	−0.4797 (5)	−0.1614 (4)	0.2594 (3)
C(21)	−0.1295 (5)	−0.2139 (3)	0.0505 (2)
C(22)	0.0681 (5)	−0.1900 (4)	0.0491 (2)
C(23)	0.1294 (6)	−0.2823 (5)	−0.0179 (3)
C(24)	−0.0102 (8)	−0.3993 (4)	−0.0827 (3)
C(25)	−0.2066 (8)	−0.4247 (4)	−0.0824 (3)
C(26)	−0.2674 (6)	−0.3328 (4)	−0.0168 (3)
C(31)	0.0242 (4)	0.0288 (3)	0.2322 (2)
C(32)	0.1327 (5)	0.1436 (3)	0.2095 (2)
C(33)	0.3098 (5)	0.2328 (3)	0.2765 (3)
C(34)	0.3819 (5)	0.2108 (3)	0.3694 (3)
C(35)	0.2786 (5)	0.0987 (3)	0.3935 (2)
C(36)	0.0985 (4)	0.0087 (3)	0.3254 (2)
H(12)	−0.1581	−0.3239	0.2073
H(13)	−0.2817	−0.4412	0.3124
H(14)	−0.5341	−0.3843	0.3814
H(15)	−0.6531	−0.2078	0.3507
H(16)	−0.5321	−0.0899	0.2461
H(22)	0.1643	−0.1093	0.0945
H(23)	0.2662	−0.2645	−0.0186
H(24)	0.0306	−0.4630	−0.1283
H(25)	−0.3019	−0.5060	−0.1275
H(26)	−0.4049	−0.3507	−0.0174
H(32)	0.0832	0.1596	0.1473
H(33)	0.3817	0.3082	0.2596
H(34)	0.5015	0.2725	0.4195
H(35)	0.3294	0.0831	0.4556
H(36)	0.0268	−0.0662	0.3427

[a] B = 6.0 Å^2 for all hydrogen atoms.

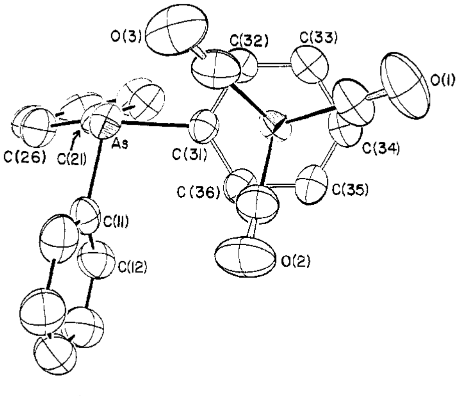

Figure 1. The $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ molecule projected onto the plane of the η^6-phenyl ring (ORTEP-II diagram; 30% ellipsoids). Hydrogen atoms have been omitted for the sake of clarity.

Calcd: Cr, 11.8; C, 57.0; H, 3.4. Found: Cr, 11.7; C, 57.8; H, 3.8. The complex was further characterized via a single-crystal X-ray diffraction study (vide infra).

Preparation of $(NMe_3)Cr(CO)_5$. A solution of $(CH_3)_3NO$ (0.35 g in 10 mL of CH_2Cl_2) was added slowly, with stirring under argon, to a solution of $Cr(CO)_6$ (1.0 g in 40 mL of THF). The resulting solution immediately turned yellow but gradually became brown-green. Vigorous bubbling accompanied the reaction as CO_2 was evolved. After 1 h, the solvent was stripped off and hexane (15 mL) was added. The solution was filtered, and the resulting orange solution was stored overnight at ~0 °C, yielding yellow needles: mp 75–76 °C (reported 76 °C[9]); ν(CO) (hexane) 2070 (w), 1933 (s), 1915 (m) cm^{-1}.

Preparation of $(OC)_3Cr[(\eta^6\text{-}C_6H_5)(C_6H_5)_2As]Cr(CO)_5$. A mixture of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ (0.1 g) and $(NMe_3)Cr(CO)_5$ (0.1 g) in hexane was stirred under argon at room temperature for 24 h. Slow removal of solvent yielded 0.02 g of orange crystals, which were washed with pentane and dried in vacuo; mp (in vacuo) 152–153 °C. IR(hexane): ν(CO) 2065 (w), 1985 (s), 1943 (s), 1922 (s) cm^{-1}.

Preparation of $[As(C_6H_5)_3]Cr(CO)_5$. This was prepared by the procedure of Connor et al.[10] IR(decane): ν(CO) 2067 (w), 1946 (s) cm^{-1}.[11]

Collection of X-ray Diffraction Data. An irregularly shaped fragment of approximate dimensions 0.23 × 0.23 × 0.30 mm was cleaved from a larger crystal. This was sealed into a thin-walled glass capillary and mounted on a Syntex P2$_1$ automated diffractometer, where crystal alignment, determination of unit-cell constants, and data collection were carried out as we have described previously;[12] details are presented in Table I.

Solution and Refinement of the Structure. All calculations were performed by using the SUNYAB modified version of the Syntex XTL program package. Redundant data were averaged (R_I = 0.7% for 245 averaged pairs), corrected for Lorentz, polarization, and absorption effects, and placed on an approximate absolute scale via a Wilson plot. The structure was then solved by direct methods using the program MULTAN which yielded the coordinates of the chromium and arsenic atoms. Subsequent difference-Fourier calculations located all remaining nonhydrogen atoms. All hydrogen atoms were then included in calculated positions based on idealized sp^2 geometry and d(C–H) = 0.95 Å.[13] Each hydrogen atom was assigned an isotropic thermal parameter of B = 6.0 Å^2. At convergence the residuals were R_F = 3.7%, R_{wF} = 3.5%, and GOF = 1.20 for all 2676 data and R_F = 2.8% and R_{wF} = 3.4% for those 2355 data with $F_o > 3\sigma(|F_o|)$. A final difference-Fourier synthesis had as its largest feature a peak of height 0.36 e Å^{-3} close to the position of the arsenic atom.

There was no evidence of secondary extinction. Analysis of the residuals in terms of magnitude of $|F_o|$, $(\sin\theta)/\lambda$, Miller indices, or

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Table III. Final Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	3.28 (2)	2.81 (2)	3.47 (2)	0.75 (2)	1.37 (2)	0.78 (2)
As	3.72 (2)	3.91 (2)	3.48 (2)	1.255 (12)	0.375 (12)	0.655 (12)
C(1)	4.3 (2)	3.9 (2)	5.9 (2)	0.88 (14)	2.70 (15)	0.66 (15)
O(1)	7.3 (2)	3.61 (12)	9.5 (2)	−0.13 (11)	3.61 (15)	−1.17 (13)
C(2)	4.5 (2)	4.3 (2)	4.6 (2)	1.42 (13)	1.82 (14)	1.42 (14)
O(2)	7.3 (2)	8.3 (2)	6.66 (15)	2.76 (13)	4.40 (14)	3.91 (14)
C(3)	4.7 (2)	5.1 (2)	4.9 (2)	2.28 (14)	2.76 (14)	2.03 (14)
O(3)	5.90 (15)	10.2 (2)	8.4 (2)	5.14 (13)	3.50 (13)	4.8 (2)
C(11)	3.45 (14)	3.62 (15)	3.30 (14)	0.44 (12)	0.68 (11)	−0.04 (11)
C(12)	5.2 (2)	3.7 (2)	5.3 (2)	0.99 (14)	1.74 (15)	0.77 (14)
C(13)	8.1 (3)	3.8 (2)	5.4 (2)	0.6 (2)	1.9 (2)	0.98 (15)
C(14)	7.6 (3)	6.4 (2)	4.0 (2)	−1.1 (2)	2.5 (2)	0.4 (2)
C(15)	5.8 (2)	8.5 (3)	5.0 (2)	1.5 (2)	2.7 (2)	0.8 (2)
C(16)	4.5 (2)	6.0 (2)	4.2 (2)	1.78 (15)	1.12 (14)	0.24 (15)
C(21)	4.6 (2)	4.2 (2)	2.64 (13)	1.52 (13)	0.60 (12)	0.89 (12)
C(22)	5.0 (2)	5.7 (2)	3.51 (15)	2.12 (15)	0.59 (13)	0.38 (14)
C(23)	6.5 (2)	7.9 (3)	4.9 (2)	4.1 (2)	1.9 (2)	1.5 (2)
C(24)	10.6 (3)	6.0 (2)	3.9 (2)	5.0 (2)	2.7 (2)	1.3 (2)
C(25)	9.1 (3)	4.4 (2)	3.9 (2)	1.4 (2)	1.3 (2)	0.17 (15)
C(26)	5.8 (2)	5.1 (2)	4.0 (2)	0.9 (2)	0.98 (15)	0.21 (15)
C(31)	3.70 (14)	2.99 (13)	3.07 (13)	1.20 (11)	0.74 (11)	0.50 (11)
C(32)	4.3 (2)	4.20 (15)	3.47 (14)	1.67 (13)	1.90 (12)	1.16 (12)
C(33)	3.68 (15)	3.75 (15)	4.9 (2)	1.07 (12)	2.17 (14)	1.00 (13)
C(34)	2.87 (14)	4.1 (2)	5.3 (2)	0.88 (12)	1.00 (13)	0.25 (14)
C(35)	4.2 (2)	4.0 (2)	3.83 (15)	1.56 (13)	0.15 (12)	0.71 (13)
C(36)	3.99 (15)	2.83 (13)	3.75 (14)	1.01 (11)	0.80 (12)	0.71 (11)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

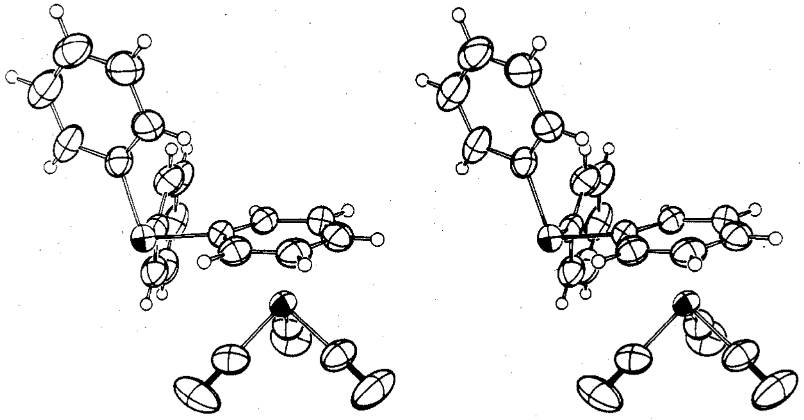

Figure 2. Stereoscopic view of the $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ molecule.

sequence number showed no specific trends.

Final positional and thermal parameters for all atoms are collected in Tables II and III.

Description of the Structure

The atomic-labeling scheme is shown in Figure 1, and the molecular geometry is presented as a stereoview in Figure 2. Interatomic distances and angles are collected in Tables IV and V; least-squares planes are shown in Table VI.

The molecule consists of a central chromium(0) atom linked to an η^6-phenyl ring of the triphenylarsine ligand and three carbonyl groups. The Cr···As distance of 3.730 (1) Å is clearly nonbonding.

The geometry about chromium is of the symmetrical "three-legged piano-stool" variety. The Bz[14]–Cr–CO angles range from 125.95 (12)–126.71 (11)°, while the OC–Cr–CO angles range from 87.96 (16)–89.09 (16)°. The $Cr(CO)_3$ moiety lies in a rotational conformation midway between eclipsed and staggered relative to the η^6-phenyl ring. The Cr–C(arene) bond lengths range from 2.193 (3) to 2.220 (4) Å (average = 2.211 [9] Å). The η^6-phenyl ring is planar (root-mean-square deviation from planarity = 0.005 Å; see Table VI) and the chromium atom lies −1.7077 (5) Å from this plane.

Carbon–carbon distances within the η^6-phenyl ring range from 1.390 (5) to 1.421 (5) Å, averaging 1.405 [11] Å. There is a slight tendency toward alternation of bond lengths with C(31)–C(32) = 1.421 (5) Å, C(33)–C(34) = 1.407 (5) Å, C(35)–C(36) = 1.411 (5) Å (average 1.413 [7] Å) vis â vis C(32)–C(33) = 1.390 (5) Å, C(34)–C(35) = 1.394 (5) Å, and C(36)–C(31) = 1.405 (4) Å (average = 1.396 [8] Å). There is also an associated alternation in C–C–C angles. These results are on the borderline of statistical significance but agree (both in direction and magnitude) with the results of Rees and Coppens[2] from extremely accurate low-temperature X-ray and neutron diffraction studies on $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.

Bond lengths within the "free" phenyl rings (C–C(av) = 1.377 [12] Å) are substantially shorter than those in the η^6-phenyl group, probably as a net result of electronic and thermal librational factors.

Chromium–carbonyl linkages are equivalent (range = 1.830 (4)–1.839 (4) Å; average = 1.835 [5] Å), as are the C–O

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(14) "Bz" is the centroid of the η^6-phenyl ring.

(15) Esd's of averaged quantities are enclosed in square brackets. They are calculated via the scatter formula: $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$.

Table IV. Interatomic Distances (Å) and Esd's for $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

(A) Distances from the Chromium Atom			
Cr-C(31)	2.219 (3)	Cr-C(1)	1.835 (4)
Cr-C(32)	2.196 (3)	Cr-C(2)	1.839 (4)
Cr-C(33)	2.215 (3)	Cr-C(3)	1.830 (4)
Cr-C(34)	2.211 (3)	Cr-As	3.730 (1)
Cr-C(35)	2.220 (4)	Cr-Bz[14]	1.708 (-)
Cr-C(36)	2.205 (3)		
(B) Arsenic-Carbon Distances			
As-C(11)	1.949 (3)	As-C(31)	1.966 (3)
As-C(21)	1.959 (3)		
(C) Carbon-Oxygen Distances			
C(1)-O(1)	1.155 (5)	C(3)-O(3)	1.153 (5)
C(2)-O(2)	1.151 (5)		
(D) Carbon-Carbon Distances within the $(\eta^6\text{-}C_6H_5)$ Moiety			
C(31)-C(32)	1.421 (5)	C(34)-C(35)	1.394 (5)
C(32)-C(33)	1.390 (5)	C(35)-C(36)	1.411 (5)
C(33)-C(34)	1.407 (5)	C(36)-C(31)	1.405 (4)
(E) Carbon-Carbon Distances within the $As(C_6H_5)_2$ Moiety			
C(11)-C(12)	1.386 (5)	C(21)-C(22)	1.374 (5)
C(12)-C(13)	1.380 (6)	C(22)-C(23)	1.394 (6)
C(13)-C(14)	1.377 (7)	C(23)-C(24)	1.374 (6)
C(14)-C(15)	1.352 (7)	C(24)-C(25)	1.361 (8)
C(15)-C(16)	1.377 (6)	C(25)-C(26)	1.378 (6)
C(16)-C(11)	1.381 (5)	C(26)-C(21)	1.391 (5)

Table V. Interatomic Angles (Deg) with Esd's for $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

(A) Angles about the Chromium Atom			
C(1)-Cr-C(2)	87.96 (16)	Bz-Cr-C(1)	126.20 (12)
C(2)-Cr-C(3)	89.09 (16)	Bz-Cr-C(2)	126.71 (11)
C(3)-Cr-C(1)	88.60 (17)	Bz-Cr-C(3)	125.95 (12)
(B) Angles about the Arsenic Atom			
C(11)-As-C(21)	99.40 (14)	C(31)-As-C(11)	98.33 (13)
C(21)-As-C(31)	98.21 (13)		
(C) Internal C-C-C Angles within the $\eta^6\text{-}C_6H_5$ Ring			
C(36)-C(31)-C(32)	118.27 (28)	C(33)-C(34)-C(35)	120.34 (32)
C(31)-C(32)-C(33)	121.27 (30)	C(34)-C(35)-C(36)	119.90 (30)
C(32)-C(33)-C(34)	119.58 (31)	C(35)-C(36)-C(31)	120.61 (29)
(D) Internal C-C-C Angles within the Phenyl Rings of the $As(C_6H_5)_2$ Moiety			
C(16)-C(11)-C(12)	118.37 (32)	C(26)-C(21)-C(22)	118.37 (33)
C(11)-C(12)-C(13)	120.67 (35)	C(21)-C(22)-C(23)	120.96 (36)
C(12)-C(13)-C(14)	119.58 (40)	C(22)-C(23)-C(24)	119.24 (41)
C(13)-C(14)-C(15)	120.26 (44)	C(23)-C(24)-C(25)	120.59 (45)
C(14)-C(15)-C(16)	120.56 (44)	C(24)-C(25)-C(26)	120.72 (37)
C(15)-C(16)-C(11)	120.55 (37)	C(25)-C(26)-C(21)	120.12 (42)
(E) Chromium-Carbon-Oxygen Angles			
Cr-C(1)-O(1)	179.33 (35)	Cr-C(3)-O(3)	178.33 (34)
Cr-C(2)-O(2)	179.61 (33)		

Table VI. Pertinent Least-Squares Planes[a] and Atomic Deviations Therefrom for $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

Deviations (Å) from Planes

atom	dev	atom	dev
(A) $-0.4197X - 0.4361Y - 0.7970Z = 0.0157$			
C(11)*	−0.002 (3)	C(14)*	0.004 (4)
C(12)*	0.002 (4)	C(15)*	−0.004 (5)
C(13)*	−0.003 (4)	C(16)*	0.003 (4)
(B) $-0.1423X + 0.7182Y - 0.6811Z = -2.0967$			
C(21)*	−0.002 (3)	C(24)*	−0.002 (4)
C(22)*	−0.002 (4)	C(25)*	−0.003 (4)
C(23)*	0.004 (5)	C(26)*	0.004 (3)
(C) $0.7830X - 0.4552Y - 0.4238Z = -1.4363$			
C(31)*	0.005 (3)	C(34)*	−0.005 (4)
C(32)*	−0.003 (3)	C(35)*	0.006 (4)
C(33)*	0.003 (3)	C(36)*	−0.006 (3)
Cr	−1.7077 (5)	As	−0.1112 (3)
C(1)	−2.798 (4)	C(3)	−2.773 (4)
O(1)	−3.494 (3)	O(3)	−3.431 (3)
C(2)	−2.809 (4)		
O(2)	−3.498 (3)		
Dihedral Angles (Deg)			
A-B	73.20	B-C	98.60
A-C	77.93		

[a] Equations of planes are expressed in orthonormal (Å) coordinates. Atoms marked with asterisks were assigned unit weight; all others were given zero weight.

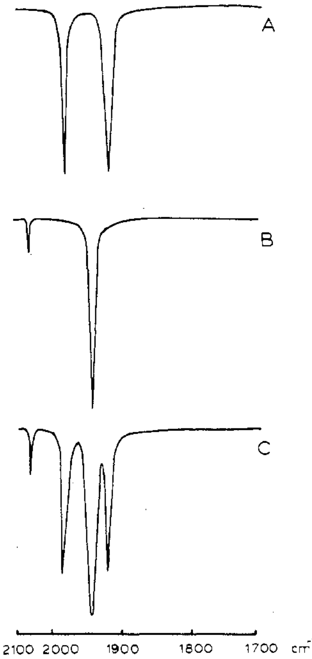

Figure 3. Infrared spectra (carbonyl stretching region) for (A) $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$, (B) $[As(C_6H_5)_3]Cr(CO)_5$, and (C) $(OC)_3Cr[(\eta^6\text{-}C_6H_5)(C_6H_5)_2As]Cr(CO)_5$.

distances (range = 1.151 (5)–1.155 (5) Å; average = 1.153 [2] Å); the Cr–C–O systems are all close to linear (178.33 (34) → 179.61 (33)°).

Discussion

The arsenic atom in $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ retains its basicity toward a metal atom as is shown by the observed reaction (1). This reaction occurs readily at room temperature.

$$[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3 + (NMe_3)Cr(CO)_5 \rightarrow (OC)_3Cr[(\eta^6\text{-}C_6H_5)(C_6H_5)_2As]Cr(CO)_5 + NMe_3 \quad (1)$$

The infrared spectrum of the binuclear product (Figure 3, spectrum C) is essentially equivalent to the composite of the spectra of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ (spectrum A) and $[As(C_6H_5)_3]Cr(CO)_5$ (spectrum B). The minor differences are (i) the absorptions from the $Cr(CO)_3$ moiety in spectrum C are shifted by approximately 7 cm^{-1} to a higher frequency relative to spectrum A and (ii) the E-mode of the $Cr(CO)_5$ moiety in the binuclear derivative (spectrum C) is broadened somewhat relative to the E-mode in $[As(C_6H_5)_3]Cr(CO)_5$ (spectrum B).

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Registry No. $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$, 74096-94-9; $(OC)_3Cr[(\eta^6\text{-}C_6H_5)(C_6H_5)_2As]Cr(CO)_5$, 74096-95-0; $(NMe_3)Cr(CO)_5$, 15228-26-9; $[As(C_6H_5)_3]Cr(CO)_5$, 29742-98-1; $Cr(CO)_6$, 13007-92-6; $(CH_3)_3NO$, 1184-78-7.

Supplementary Material Available: A list of observed and calculated structure factor amplitudes and data-processing formulas (16 pages). Ordering information is given on any current masthead page.