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Formation of an Arsinidene Complex of Chromium via As–C Bond Cleavage. Further Reaction To Form a $CrAs_4$ Heterometallocycle. Synthesis and X-ray Structures of $[Cr(CO)_5]_2$(*μ*-*t*-BuAs) and (CO)$_4$CrAs-*t*-BuCl(*t*-BuAs)$_2$As-*t*-BuCl

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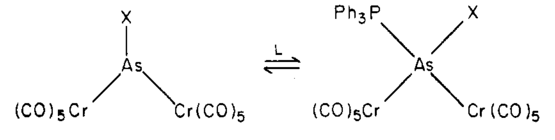
Reaction of $Na_2Cr_2(CO)_{10}$ with *t*-Bu_2AsCl in THF yields blue-green crystalline $[Cr(CO)_5]_2$(*μ*-*t*-BuAs) (3) in ca. 60% yield. The X-ray crystal structure of 3 shows an arsinidene (*t*-BuAs) unit bridging two $Cr(CO)_5$ units with no Cr–Cr bond (Cr–Cr = 4.315 (2) Å). The reaction mixture containing 3, in the presence of PPN^+Cl^-, gives a mononuclear Cr(0) complex containing a $CrAs_4$ heterometallocycle; (CO)$_4$CrAs-*t*-BuCl(As-*t*-Bu)$_2$As-*t*-BuCl (4) in ca. 12% yield. Crystal data for 3: $C_{14}H_9O_{10}AsCr_2$, M_r = 516.06, triclinic, $P\bar{1}$, a = 9.397 (3) Å, b = 9.483 (3) Å, c = 11.778 (5) Å, α = 87.86 (4)°, β = 70.67 (3)°, γ = 77.77 (3)°, U = 967.3 (5) Å^3, D_{calcd} = 1.593 g cm^{-3}, Z = 2, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 15.43 cm^{-1}, final R = 0.047, R_w = 0.055 from 2804 observed reflections (3617 measured). Crystal data for 4: $C_{20}H_{36}As_4Cl_2CrO_4$, M_r = 763.10, monoclinic, $P2_1/n$, a = 11.0295 (18) Å, b = 35.190 (5) Å, c = 15.303 (3) Å, β = 97.815 (15)°, U = 5884.5 (3) Å^3, D_{calcd} = 1.723 g cm^{-3}, Z = 8, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 53.2 cm^{-1}, final R = 0.054, R_w = 0.073 from 4100 observed reflections (11533 measured).

Introduction

Examples of phosphinidene (RP^{2-}),[1] arsinidene (RAs^{2-}),[2-8] or stibinidene (RSb^{2-})[9] units which bridge two or more transition metals are known for a variety of systems. There are a relatively large number of complexes containing phosphinidene units compared to those with arsinidene or stibinidene groups.

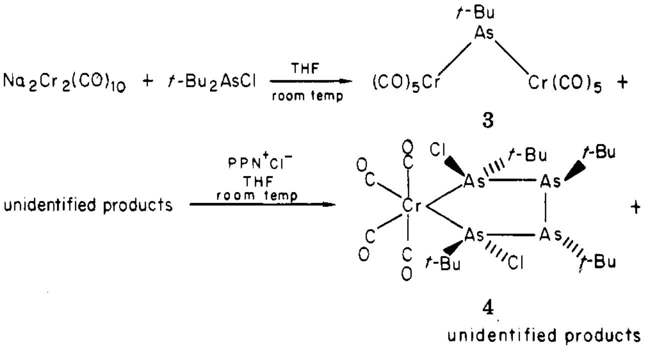
Of revelance to this report is the work of Huttner and co-workers who have reported the synthesis and structures of several dinuclear chromium arsinidene-bridged complexes of formula $[Cr(CO)_5]_2$(*μ*-AsX) (1, X = Ph, Cl, *t*-Bu, *i*-Bu; see Scheme I).[2-8,25] These complexes contain a coordinatively unsaturated arsenic bridging two transition-metal centers. The trigonal-planar coordinated arsenic atom is susceptible to attack by Lewis bases. This has been demonstrated by the isolation and characterization of the arsindiylphosphorane complex 2.[5] As part of a study of the steric effects of bulky phosphido (R_2P^-) and arsenido (R_2As^-) groups as ligands for d-block transition metals, we have used the di-*tert*-butylphosphido unit (*t*-Bu_2P^-) and isolated and characterized a number of new complexes.[10] In order to see if the analogous arsenic ligand *t*-Bu_2As^- would also provide interesting new complexes, we examined the reaction of $Cr_2(CO)_{10}{}^{2-}$ with 2 equiv of *t*-Bu_2AsCl in Et_2O expecting to synthesize a dichromium, *t*-Bu_2As^--bridged compound. Surprisingly, however, under the reaction conditions employed, the complex formed in high yield is $[Cr(CO)_5]_2$(*μ*-*t*-BuAs) (3). The formation of 3 must occur via an As–C bond cleavage which has also been observed in thermal reactions involving organoarsenic species and metal carbonyls.[11]



(1)

1, X = Ph, Cl, *t*-Bu, *i*-Bu 2, X = Cl; L = PPh$_3$ (only)

Scheme I



In the presence of excess PPN^+Cl^- ((*μ*-nitrido)bis(triphenylphosphorus)chloride), the reaction mixture con-

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[11] See for example: Sullivan, P. J.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1547 and references therein.

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Table I. Details of Data Collection, Solution Structure, and Refinement for 3 and 4

formula	$C_{14}H_9AsCr_2O_{10}$ (3)	$C_{20}H_{36}As_4Cl_2CrO_4$ (4)
mol wt	516.06	763.10
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14)
cell constants		
a, Å	9.379 (3)	11.0295 (18)
b, Å	9.483 (3)	35.190 (5)
c, Å	11.778 (5)	15.303 (3)
α, deg	87.86 (4)	
β, deg	70.67 (3)	97.815 (15)
γ, deg	77.77 (3)	
cell vol, $Å^3$	967.3 (5)	5884.5 (3)
molecules/unit cell	2	8
D_{calcd}, g cm^{-3}	1.593	1.723
μ(calcd), cm^{-1}	15.43	53.2
radiation, Å	Mo Kα, 0.710 69	Mo Kα, 0.710 69
max cryst dimens, mm	0.30 × 0.35 × 0.25	0.40 × 0.25 × 0.20
scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.35 tan θ
std reflctns	$02\bar{1}$, $21\bar{5}$	049, $\bar{6}9\bar{1}$
decay of stds	−1.9%	−1.0%
reflctns measd	3617	11533
2θ range, deg	2–50	2–50
reflctns obsd, $I > 3\sigma(I)$	2804	4100
no. of parameters varied	271	549
data/parameter ratio	10.35	7.47
R	0.047	0.054
R_w	0.055	0.073

taining 3 yields several new products. Of these $(CO)_4CrAs$-t-BuCl(As-t-Bu)$_2$As-t-BuCl (4), containing an interesting $CrAs_4$ heterometallocycle, is formed in low yield and has been fully characterized. We report here full details of the synthesis, characterization, and X-ray crystal structures of 3 and 4.

Experimental Section

All reactions were performed under oxygen-free nitrogen. Microanalyses (C and H) by the Schwartzkopf Microanalytical Laboratory, Woodside, NY, were satisfactory. Tetrahydrofuran, toluene, and diethyl ether were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Instruments: IR, Perkin-Elmer 1330; NMR, Varian EM-390 (^1H, 90 MHz), Varian FT-80. Melting points were in sealed capillaries under nitrogen (1 atm) and are uncorrected. $Na_2Cr_2(CO)_{10}$[12] and t-Bu_2AsCl[13] were prepared as previously described.

$[Cr(CO)_5]_2(\mu$-t-BuAs) (3). A solution of t-Bu_2AsCl (1.5 mL, 7.0 mmol) in THF (50 mL) was added dropwise to a solution of $Na_2Cr_2(CO)_{10}$ (2.44 g, 5.68 mmol) in THF (100 mL) at room temperature. As the addition proceeded (over ca. 20 min) the solution turned from yellow to red and finally to orange. The mixture was stirred at room temperature (10 h). At this stage the color of the solution was bright yellow and it contained a small amount of a white precipitate. The solution was filtered, and volatile materials were removed under vacuum at room temperature. A dark blue-green tar was obtained that was extracted with toluene (50 mL). The solution was filtered and the volume reduced to ca. 10 mL under vacuum. Cooling (−20 °C) gave dark green crystals of 3 which were collected and dried under vacuum: yield 1.58 g (60%); melting point; the complex softens at 45 °C and finally decomposes at 144–146 °C; IR (KBr disk) 2920 (m, br), 2060 (m, sh), 2025 (sh), 1930 (vs, br), 1462 (m), 1388 (m), 1364 (m), 1258 (w), 1155 (m), 1013 (w), 792 (w), 640 (vs), 453 (m) cm^{-1} (key: s = strong, m = medium, w = weak, br = broad, sh = sharp); ^1H NMR (in C_6D_6 at 35 °C, relative to Me_4Si, δ 0.0 at 90 MHz) δ 1.08 (s, t-BuAs).

$(CO)_4CrAs$-t-BuCl(As-t-Bu)$_2$As-t-BuCl (4). A solution of t-Bu_2AsCl (5.0 mL, 23 mmol) in THF (50 mL) was added dropwise to a solution of $Na_2Cr_2(CO)_{10}$ (4.89 g, 11.36 mmol) in THF (100 mL) at room temperature. The mixture was stirred (10 h). The color changes were the same as those observed for 3 above. PPN^+Cl^- (7.15 g, 12.5 mmol) was added to the bright yellow reaction mixture which was stirred a further 2 h. The solution was then filtered, and volatile materials were removed under vacuum. The residue (a yellow tar) was extracted into toluene, and the resulting solution was filtered. Solvent was again removed under vacuum and the residue extracted into diethyl ether (30 mL). The resulting solution was filtered and the volume reduced to ca. 10 mL under vacuum. Cooling (−20 °C) gave yellow-orange crystals of 4 which were collected and dried under vacuum: yield 0.54 g, 12% based on As; melting point; the complex blackens over the range 190–200 °C but does not melt below 360 °C; IR (Nujol mull, KBr plates) 2010 (s), 1925 (vs, br), 1898 (vs, br), 1385 (m), 1360 (s), 1258 (w), 1147 (s), 1005 (m), 792 (w), 653 (s), 621 (s), 538 (w), 490 (m), 472 (m) cm^{-1}.

X-ray Experimental Data. Suitable crystals of 3 and 4 were mounted under nitrogen in thin-walled glass capillaries. Final lattice parameters were determined from 25 high-angle reflections (26° > 2θ > 28°) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of data collection were similar to those outlined in ref 14. Crystal data, collection parameters, and results of refinements for 3 and 4 are given in Table I. For 3 the structure refined successfully in $P\bar{1}$ which was therefore taken as the correct space group. For 4 the space group was uniquely defined by systematic absences as $P2_1/n$, a nonstandard setting of $P2_1/c$.

The data for 4 were corrected for absorption by an empirical psi scan method. No absorption correction was applied for 3. Data for both 3 and 4 were corrected for Lorentz and polarization effects. The structure of 3 was solved by using heavy-atom methods (Patterson), and difference Fourier maps followed by least-squares refinement. Unit weights were used throughout. All non-hydrogen atoms were refined anisotropically (hydrogen atoms had fixed isotropic temperature factors). The highest peak in the final difference Fourier was 1.23 e/$Å^3$, located 1.10 Å from Cr(1). All 12 peaks greater than 0.5 e/$Å^3$ were within 1.2 Å of the three heavy atoms.

For 4 the coordinates of all ten of the Cr and As atoms in the asymmetric unit were obtained by direct methods (MULTAN).[15] The remaining non-hydrogen atoms were located by the use of difference Fourier maps followed by least-squares refinement. The

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Table II. Positional Parameters for 3[a]

atom	x	y	z	B, Å^2
As	0.24898 (7)	0.29283 (7)	0.25754 (6)	3.00 (1)
Cr(1)	0.1343 (1)	0.5265 (1)	0.20927 (9)	2.95 (2)
Cr(2)	0.5434 (1)	0.7723 (1)	0.66148 (9)	3.44 (2)
O(1)	0.1863 (6)	0.4116 (7)	−0.0418 (4)	5.5 (1)
O(2)	−0.1976 (6)	0.4885 (7)	0.3087 (5)	5.6 (1)
O(3)	−0.0088 (7)	0.8150 (6)	0.1326 (5)	5.5 (1)
O(4)	0.0789 (6)	0.6471 (7)	0.4593 (4)	5.4 (1)
O(5)	0.4458 (6)	0.6114 (7)	0.1218 (5)	6.2 (2)
O(6)	0.2241 (7)	0.1756 (7)	0.5781 (5)	6.1 (2)
O(7)	0.5507 (7)	−0.0913 (7)	0.2698 (6)	7.2 (2)
O(8)	0.7025 (6)	0.1645 (7)	0.4585 (5)	6.1 (2)
O(9)	0.6891 (7)	0.2735 (8)	0.0980 (5)	7.5 (2)
O(10)	0.4262 (6)	0.5424 (6)	0.4001 (5)	5.7 (1)
C(1)	0.1666 (7)	0.4523 (8)	0.0528 (6)	3.6 (2)
C(2)	−0.0720 (8)	0.4952 (8)	0.2704 (6)	3.8 (2)
C(3)	0.0464 (7)	0.7077 (8)	0.1632 (6)	3.7 (2)
C(4)	0.1028 (7)	0.6016 (8)	0.3657 (6)	3.6 (2)
C(5)	0.3303 (8)	0.5764 (8)	0.1542 (6)	4.0 (2)
C(6)	0.3093 (8)	0.1963 (9)	0.4894 (6)	4.3 (2)
C(7)	0.5071 (8)	0.0299 (9)	0.2958 (7)	4.6 (2)
C(8)	0.6116 (8)	0.1890 (9)	0.4130 (7)	4.4 (2)
C(9)	0.6007 (8)	0.2572 (9)	0.1877 (6)	4.6 (2)
C(10)	0.4323 (8)	0.4236 (9)	0.3777 (6)	4.1 (2)
C(11)	0.1730 (8)	0.1232 (8)	0.2161 (6)	3.8 (2)
C(12)	0.295 (1)	0.051 (1)	0.1043 (7)	5.6 (2)
C(13)	0.1444 (9)	0.0236 (9)	0.3216 (8)	5.3 (2)
C(14)	0.0195 (9)	0.1721 (9)	0.1916 (8)	5.4 (2)
H(1)*	0.393 (7)	0.019 (7)	0.110 (6)	
H(2)*	0.311 (7)	0.122 (7)	0.043 (6)	
H(3)*	0.280 (7)	0.958 (7)	0.079 (6)	
H(4)*	0.116 (7)	0.930 (7)	0.0297 (6)	
H(5)*	0.074 (7)	0.070 (7)	0.339 (6)	
H(6)*	0.246 (7)	−0.031 (7)	0.322 (6)	
H(7)*	0.004 (7)	0.081 (7)	0.161 (6)	
H(8)*	0.061 (7)	0.779 (7)	0.719 (6)	
H(9)*	0.965 (7)	0.764 (7)	0.880 (6)	

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

H atoms were not located. Unit weights were used throughout the refinement. All non-hydrogen atoms except C(243) and C(242) of a *t*-Bu group were refined anisotropically. C(243) and C(242) were refined isotropically since they gave "nonpositive definite" temperature factors on attempted anisotropic refinement. The largest peak in the final difference Fourier was 0.87 e/Å^3, located 1.12 Å from As(11).

All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP-PLUS" (B.A. Frenz and Associates, College Station, TX 77840, 4th ed., 1981). Scattering factors were taken from ref 16.

Results and Discussion

The interaction of *t*-Bu_2AsCl with $Na_2Cr_2(CO)_{10}$ in THF at room temperature gives a bright yellow solution from which dark blue-green crystalline $[Cr(CO)_5]_2(\mu$-*t*-BuAs) (**3**) can be isolated in ca. 60% yield. Clearly further reaction to produce **3** takes place on workup. **3** is air sensitive both in the solid state and in solution and decomposes rapidly. The formation of **3** appears to occur via an As–C bond cleavage. We note that other systems involving organoarsenic systems and metal carbonyls also undergo As–C cleavage reactions.[11] It is interesting to note that **3** may also be prepared from the reaction of $Na_2Cr_2(CO)_{10}$ with *t*-$BuAsCl_2$.[7] In contrast, the reaction of $Cr_2(CO)_{10}^{2-}$ with $PhAsCl_2$ gives $[Cr(CO)_5]_3As_2Ph_2$ which contains a coordinated As=As doubly bonded unit.[17] The phenyl analogue of **3** may be prepared by demetalation of $(CO)_5CrAs(Ph)Li_2$.[3]

3 dissolves readily in hexane, toluene, THF, and diethyl ether to give intensely colored blue-green solutions which remain this color at −78 °C. This behavior is in contrast to that of the phenyl analogue $[Cr(CO)_5]_2(\mu$-PhAs) (**1**)[3] which is yellow in good donor solvents such as Et_2O or THF. This behavior for **1** has been rationalized in terms of a reversible equilibrium involving attack at the coordinatively unsaturated arsenic atom by Lewis bases (Et_2O, THF).[5] The absence of this effect for **3** may be due to the steric effect of the bulky *tert*-butyl group which may prevent attack at As by the donor solvents. Our spectroscopic data (IR, ^1H NMR) for **3** are similar to that reported previously.[7] The data are in accord with the structure as determined by a single-crystal X-ray diffraction study. Thus the ^1H NMR shows a sharp singlet (*t*-BuAs) at δ 1.08 (in C_6D_6 relative to Me_4Si, δ 0.0), and the IR shows only terminal ν_{CO} absorptions.

X-ray Crystal Structure of $[Cr(CO)_5]_2(\mu$-*t*-BuAs) (3). The complex crystallizes in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit (two per unit cell). Crystal data and the summary of intensity data collection parameters for **3** are given in Table I. Atomic positional parameters, bond lengths, and bond angles for **3** are presented in Tables II, III, and IV, respectively. A general view of the molecule with the atom numbering

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(16) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, United Kingdom, 1974; Vol. 4.

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Table III. Bond Lengths (Å) for 3[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
As	Cr(1)	2.387 (1)	Cr(2)	C(10)	1.879 (7)	C(11)	C(13)	1.518 (9)
As	Cr(2)	2.403 (1)	O(1)	C(1)	1.135 (7)	C(11)	C(14)	1.538 (9)
As	C(11)	2.027 (6)	O(2)	C(2)	1.131 (7)	C(12)	H(1)	0.93 (6)
Cr(1)	C(1)	1.903 (6)	O(3)	C(3)	1.143 (7)	C(12)	H(2)	0.97 (6)
Cr(1)	C(2)	1.915 (6)	O(4)	C(4)	1.133 (7)	C(12)	H(3)	0.99 (6)
Cr(1)	C(3)	1.885 (6)	O(5)	C(5)	1.141 (7)	C(13)	H(4)	1.05 (6)
Cr(1)	C(1)	1.907 (6)	O(6)	C(6)	1.127 (7)	C(13)	H(5)	0.90 (6)
Cr(1)	C(5)	1.895 (6)	O(7)	C(7)	1.152 (8)	C(13)	H(6)	0.99 (6)
Cr(2)	C(6)	1.915 (7)	O(8)	C(8)	1.131 (7)	C(14)	H(7)	1.00 (6)
Cr(2)	C(7)	1.879 (7)	O(9)	C(9)	1.136 (7)	C(14)	H(8)	1.12 (6)
Cr(2)	C(8)	1.903 (7)	O(10)	C(10)	1.152 (7)	C(14)	H(9)	1.00 (6)
Cr(2)	C(9)	1.897 (7)	C(11)	C(12)	1.503 (9)			

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

Table IV. Bond Angles (deg) for 3[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cr(1)	As	Cr(2)	128.54 (4)	Cr(1)	C(2)	O(2)	174.3 (6)
Cr(1)	As	C(11)	116.8 (2)	Cr(1)	C(3)	O(3)	177.5 (5)
Cr(2)	As	C(11)	114.5 (2)	Cr(1)	C(4)	O(4)	177.6 (5)
As	Cr(1)	C(1)	89.1 (2)	Cr(1)	C(5)	O(5)	177.6 (6)
As	Cr(1)	C(2)	94.4 (2)	Cr(2)	C(6)	O(6)	178.8 (6)
As	Cr(1)	C(3)	177.1 (2)	Cr(2)	C(7)	O(7)	174.1 (6)
As	Cr(1)	C(4)	91.0 (2)	Cr(2)	C(8)	O(8)	178.9 (6)
As	Cr(1)	C(5)	90.1 (2)	Cr(2)	C(9)	O(9)	178.7 (6)
C(1)	Cr(1)	C(2)	92.8 (2)	Cr(2)	C(10)	O(10)	176.2 (6)
C(1)	Cr(1)	C(3)	88.1 (3)	As	C(11)	C(12)	106.3 (5)
C(1)	Cr(1)	C(4)	179.6 (3)	As	C(11)	C(13)	109.6 (4)
C(1)	Cr(1)	C(5)	90.4 (2)	As	C(11)	C(14)	111.8 (4)
C(2)	Cr(1)	C(3)	86.0 (3)	C(12)	C(11)	C(13)	112.7 (6)
C(2)	Cr(1)	C(4)	87.5 (2)	C(12)	C(11)	C(14)	109.4 (6)
C(2)	Cr(1)	C(5)	174.5 (3)	C(13)	C(11)	C(14)	107.0 (6)
C(3)	Cr(1)	C(4)	91.8 (3)	C(11)	C(12)	H(1)	116 (4)
C(3)	Cr(1)	C(5)	89.6 (3)	C(11)	C(12)	H(2)	108 (4)
C(4)	Cr(1)	C(5)	89.3 (2)	C(11)	C(12)	H(3)	116 (4)
As	Cr(2)	C(6)	88.7 (2)	H(1)	C(12)	H(2)	103 (5)
As	Cr(2)	C(7)	96.8 (2)	H(1)	C(12)	H(3)	99 (5)
As	Cr(2)	C(8)	175.0 (2)	H(2)	C(12)	H(3)	115 (5)
As	Cr(2)	C(9)	90.5 (2)	C(11)	C(13)	H(4)	110 (3)
As	Cr(2)	C(10)	89.1 (2)	C(11)	C(13)	H(5)	112 (4)
C(6)	Cr(2)	C(7)	91.3 (3)	C(11)	C(13)	H(6)	107 (3)
C(6)	Cr(2)	C(8)	88.6 (3)	H(4)	C(13)	H(5)	113 (5)
C(6)	Cr(2)	C(9)	179.0 (3)	H(4)	C(13)	H(6)	92 (5)
C(6)	Cr(2)	C(10)	92.8 (3)	H(5)	C(13)	H(6)	121 (5)
C(7)	Cr(2)	C(8)	87.4 (3)	C(11)	C(14)	H(7)	104 (3)
C(7)	Cr(2)	C(9)	88.1 (3)	C(11)	C(14)	H(8)	102 (3)
C(7)	Cr(2)	C(10)	172.9 (3)	C(11)	C(14)	H(9)	109 (3)
C(8)	Cr(2)	C(9)	92.2 (3)	H(7)	C(14)	H(8)	119 (5)
C(8)	Cr(2)	C(10)	86.9 (3)	H(7)	C(14)	H(9)	104 (5)
C(9)	Cr(2)	C(10)	87.9 (3)	H(8)	C(14)	H(9)	118 (5)
Cr(1)	C(1)	O(1)	178.1 (6)				

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

scheme is shown in Figure 1. The structure consists of discrete molecules with no short intermolecular contacts.

Several features of the structure are worthy of comment. The coordination around the As atom is virtually planar[18] (sum of angles about As is 359.84°), and if one considers the As atom to be donating two electrons to each Cr (giving 18-electron Cr atoms), then it is electron deficient (six electrons). This may be partially compensated for by $\mathrm{Cr}_{\mathrm{d}\pi} \rightarrow \mathrm{As}_{\mathrm{p}\pi}$ back-bonding since the As–Cr distances are significantly shorter than those observed in either dialkyl arsenido-bridged complexes or in terminally bonded arsine ligands (Cr(1)–As = 2.387 (1) Å, Cr(2)–As = 2.403 (1) Å). These distances are similar to those found in the phenyl analogue (average Cr–As = 2.38 Å) which also has a planar geometry about As.

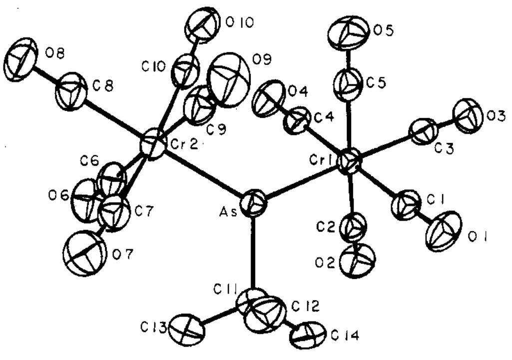

Figure 1. General view of $[\mathrm{Cr(CO)_5}]_2(\mu\text{-}t\text{-BuAs})$ (3).

The methyl groups of the μ-*t*-BuAs unit are aligned so that intramolecular contacts with the carbonyl groups are minimized. Thus C(14) of the *t*-BuAs group is oriented

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[18] Distances (Å) from least-squares plane formed by Cr(1), Cr(2), As, and C(11): Cr(1), -0.04; Cr(2), -0.03; C(11), -0.14, As, 0.21.

Table V. Positional Parameters for 4

atom	*x*	*y*	*z*	*B*, Å^2
Cr(1)	0.1298 (3)	0.9886 (1)	0.3150 (2)	3.17 (7)
As(11)	0.7197 (2)	0.03732 (6)	0.7695 (1)	2.94 (4)
As(12)	0.4171 (2)	0.00549 (6)	0.1603 (1)	3.06 (4)
As(13)	0.6240 (2)	−0.06752 (6)	0.7809 (1)	2.88 (4)
As(14)	0.2128 (2)	0.05220 (6)	0.3100 (1)	2.95 (4)
Cl(11)	0.0972 (6)	0.4236 (2)	0.1856 (4)	5.3 (2)
Cl(14)	0.0618 (6)	0.0913 (2)	0.2663 (5)	7.1 (2)
C(11)	0.267 (2)	0.4776 (5)	0.080 (1)	3.2 (5)
O(11)	0.207 (2)	0.4685 (5)	0.018 (1)	5.7 (4)
C(12)	0.511 (2)	0.4920 (8)	0.876 (1)	5.0 (6)
O(12)	0.432 (2)	0.4793 (7)	0.912 (1)	9.1 (6)
C(13)	0.980 (2)	0.0016 (7)	0.791 (1)	4.8 (6)
O(13)	0.451 (1)	0.4978 (6)	0.647 (1)	7.6 (5)
C(14)	0.437 (2)	0.4423 (7)	0.171 (2)	6.5 (6)
O(14)	0.482 (2)	0.4135 (5)	0.158 (1)	9.3 (6)
C(110)	0.263 (2)	0.4270 (8)	0.371 (1)	5.7 (7)
C(111)	0.335 (2)	0.4509 (9)	0.446 (2)	6.6 (7)
C(112)	0.146 (2)	0.4094 (9)	0.401 (2)	6.9 (7)
C(113)	0.337 (3)	0.3927 (8)	0.334 (2)	11.0 (9)
C(120)	0.091 (2)	0.5006 (7)	0.719 (2)	5.0 (6)
C(121)	0.104 (2)	0.495 (1)	0.823 (2)	9 (1)
C(122)	0.363 (2)	0.0392 (8)	0.808 (2)	7.0 (7)
C(123)	0.166 (2)	0.469 (1)	0.680 (3)	12 (1)
C(130)	0.292 (2)	0.0926 (7)	0.105 (1)	4.0 (5)
C(131)	0.396 (2)	0.0949 (7)	0.048 (1)	5.6 (6)
C(132)	0.181 (2)	0.0679 (8)	0.060 (2)	6.1 (7)
C(133)	0.262 (2)	0.1330 (7)	0.130 (2)	5.9 (7)
C(140)	0.278 (2)	0.0806 (5)	0.421 (1)	3.9 (5)
C(141)	0.291 (3)	0.1229 (7)	0.400 (2)	6.9 (7)
C(142)	0.404 (2)	0.0623 (9)	0.453 (1)	5.8 (7)
C(143)	0.185 (2)	0.0751 (6)	0.486 (1)	6.5 (6)
Cr(2)	0.1608 (3)	0.2374 (1)	0.8863 (2)	3.44 (8)
As(21)	0.3190 (2)	0.21200 (6)	0.8078 (1)	2.80 (4)
As(22)	0.9542 (2)	0.24580 (6)	0.2347 (1)	2.83 (4)
As(23)	0.3846 (2)	0.31684 (6)	0.7700 (1)	2.93 (4)
As(24)	0.2206 (2)	0.30244 (6)	0.8614 (1)	3.30 (5)
Cl(21)	0.4431 (6)	0.1764 (2)	0.9002 (4)	5.0 (1)
Cl(24)	0.0564 (6)	0.3323 (2)	0.7982 (5)	7.0 (2)
C(21)	0.036 (2)	0.2574 (8)	0.944 (1)	5.2 (6)
O(21)	0.958 (2)	0.2670 (7)	0.979 (1)	8.9 (6)
C(22)	0.267 (2)	0.2338 (7)	−0.005 (1)	5.0 (6)
O(22)	0.328 (2)	0.2303 (5)	0.060 (1)	7.0 (5)
C(23)	0.049 (2)	0.2390 (7)	0.782 (1)	4.6 (6)
O(23)	0.473 (2)	0.2629 (6)	0.225 (1)	7.4 (6)
C(24)	0.114 (2)	0.1885 (8)	0.911 (1)	5.7 (6)
O(24)	0.076 (2)	0.1607 (5)	0.927 (1)	7.7 (5)
C(210)	0.287 (2)	0.1724 (8)	0.710 (2)	6.7 (7)
C(211)	0.214 (2)	0.1950 (7)	0.630 (2)	5.6 (6)
C(212)	0.407 (2)	0.1557 (7)	0.687 (2)	5.0 (6)
C(213)	0.206 (3)	0.1427 (7)	0.741 (2)	7.1 (8)
C(220)	0.123 (2)	0.2454 (7)	0.309 (2)	4.3 (6)
C(221)	0.118 (2)	0.2368 (9)	0.408 (1)	6.2 (8)
C(222)	0.194 (2)	0.2135 (8)	0.266 (2)	5.4 (6)
C(223)	0.183 (2)	0.2852 (8)	0.296 (2)	6.8 (7)
C(230)	0.299 (2)	0.3316 (6)	0.648 (1)	4.1 (5)
C(231)	0.200 (3)	0.3057 (7)	0.612 (2)	6.1 (7)
C(232)	0.251 (2)	0.3740 (6)	0.659 (2)	5.2 (6)
C(233)	0.402 (2)	0.3315 (7)	0.590 (1)	5.3 (6)
C(240)	0.270 (2)	0.3399 (6)	0.959 (1)	5.2 (6)
C(241)	0.396 (3)	0.3264 (9)	0.007 (2)	6.6 (7)
C(242)*	0.274 (2)	0.3811 (7)	0.921 (2)	5.3 (5)
C(243)*	0.173 (3)	0.3369 (9)	0.025 (2)	6.7 (7)

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

between carbonyls C(1)–O(1) and C(2)–O(2) of Cr(1) and C(7)–O(7) of Cr(2) fits between C(13) and C(12) of the *t*-Bu group. The close H–C or H–O distances involved average ca. 2.57 Å.[19] This feature results in a twisting of the equatorial CO units of Cr(1) relative to the Cr_2As plane. Figure 2 shows this effect with a view virtually along the Cr–Cr vector. Thus Cr(1)–C(2)–O(2) is inclined 46° relative to the Cr(1)–Cr(2)–As–C(11) plane while C(7)—O(7) and C(10)–O(10) are more closely aligned to this plane (8°). The inclination of Cr(1)–C(2)–O(2) may be compared to an analogous angle of 27° in $[Cr(CO)_5]_2(\mu\text{-PhAs})$.[4]

Rearrangement of $[Cr(CO)_5]_2(\mu\text{-}t\text{-BuAs})$ in the

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[19] Close interactions (Å): H(6) (on C(13)) is 2.55 from C(7); H(9) (on C(14)) is 2.58 from C(1); H(8) (on C(14)) is 2.58 from C(2) and 2.57 from O(2).

Table VI. Bond Lengths (Å) for One Molecule of 4

atom 1	atom 2	dist	atom 1	atom 2	dist
Cr(1)	As(11)	2.418 (1)	C(12)	O(12)	1.178 (10)
Cr(1)	As(14)	2.422 (1)	C(13)	O(13)	1.136 (9)
Cr(1)	C(11)	1.885 (8)	C(14)	O(14)	1.156 (10)
Cr(1)	C(12)	1.843 (10)	C(110)	C(111)	1.553 (12)
Cr(1)	C(13)	1.919 (9)	C(110)	C(112)	1.562 (12)
Cr(1)	C(14)	1.814 (9)	C(110)	C(113)	1.599 (14)
As(11)	As(12)	2.478 (1)	C(120)	C(121)	1.597 (12)
As(11)	Cl(11)	2.213 (2)	C(120)	C(122)	1.519 (11)
As(11)	C(110)	2.004 (8)	C(120)	C(123)	1.553 (14)
As(12)	As(13)	2.427 (1)	C(130)	C(131)	1.522 (10)
As(12)	C(120)	2.016 (7)	C(130)	C(132)	1.580 (12)
As(13)	As(14)	2.479 (1)	C(130)	C(133)	1.522 (11)
As(13)	C(130)	2.065 (7)	C(140)	C(141)	1.536 (11)
As(14)	Cl(14)	2.193 (2)	C(140)	C(142)	1.549 (11)
As(14)	C(140)	2.021 (6)	C(140)	C(143)	1.532 (10)
C(11)	O(11)	1.126 (8)			

Presence of PPN$^+$Cl$^-$. Formation of (CO)$_4$CrAs-*t*-BuCl(As-*t*-Bu)$_2$As-*t*-BuCl (4). Generation of the initial yellow solution from which (3) may be isolated followed by the addition of a large excess of PPN$^+$Cl$^-$ ((Ph$_3$P)$_2$N$^+$Cl$^-$; (μ-nitrido)bis(triphenylphosphorus)-chloride) results in a solution of similar color to that obtained in the absence of PPN$^+$Cl$^-$. However, removal of solvent results in an orange residue instead of a blue-green one. From this residue we have so far isolated and characterized a mononuclear Cr(0) complex containing an unusual CrAs$_4$ heterometallocycle: (CO)$_4$CrAs-*t*-BuCl-(As-*t*-Bu)$_2$As-*t*-BuCl (4) in ca. 12% yield based on As. The latter complex is an orange crystalline material which can be handled for several minutes in air without decomposition. Spectroscopic data (IR, ^{1}NMR; see Experimental Section) is consistent with the structure as determined by X-ray crystallography. It consists of a five-membered CrAs$_4$ ring in which an As-*t*-BuCl(As-*t*-Bu)$_2$As-*t*-BuCl unit functions as a chelating bidentate four-electron donor via

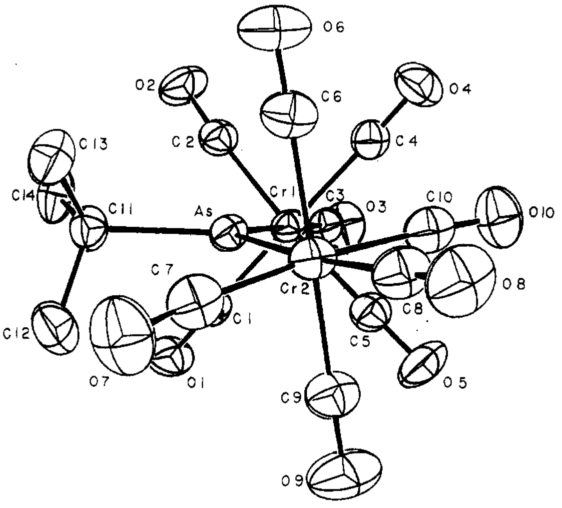

Figure 2. View of 3 showing intramolecular packing and staggering of equatorial CO units relative to the Cr$_2$As plane.

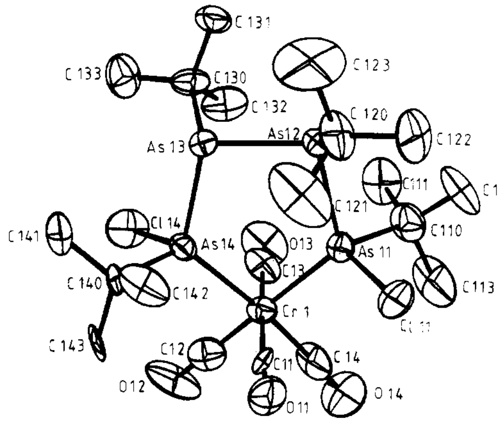

Figure 3. General view of (CO)$_4$CrAs-*t*-BuCl(As-*t*-Bu)$_2$As-*t*-BuCl (4).

Table VII. Bond Angles (deg) for One Molecule of 4

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
As(11)	Cr(1)	As(14)	92.43 (5)	C(131)	C(130)	C(132)	112.7 (7)
As(11)	Cr(1)	C(11)	90.1 (2)	C(131)	C(130)	C(133)	107.3 (7)
As(11)	Cr(1)	C(12)	177.8 (2)	C(132)	C(130)	C(133)	116.0 (7)
As(11)	Cr(1)	C(13)	91.0 (2)	As(14)	C(140)	C(141)	109.5 (5)
As(11)	Cr(1)	C(14)	92.5 (3)	As(14)	C(140)	C(142)	104.9 (5)
As(14)	Cr(1)	C(11)	91.7 (2)	As(14)	C(140)	C(143)	107.0 (5)
As(14)	Cr(1)	C(12)	88.4 (3)	C(141)	C(140)	C(142)	111.2 (8)
As(14)	Cr(1)	C(13)	90.4 (3)	C(141)	C(140)	C(143)	110.6 (7)
As(14)	Cr(1)	C(14)	174.2 (3)	C(111)	C(110)	C(112)	110.8 (8)
C(11)	Cr(1)	C(12)	91.9 (3)	As(12)	As(11)	C(110)	98.1 (3)
C(11)	Cr(1)	C(13)	177.6 (3)	Cl(11)	As(11)	C(110)	97.1 (3)
C(11)	Cr(1)	C(14)	85.3 (4)	As(11)	As(12)	As(13)	103.32 (4)
C(12)	Cr(1)	C(13)	87.0 (3)	As(11)	As(12)	C(120)	110.0 (3)
C(12)	Cr(1)	C(14)	86.8 (4)	As(13)	As(12)	C(120)	98.5 (2)
C(13)	Cr(1)	C(14)	92.5 (4)	As(12)	As(13)	As(14)	101.50 (4)
Cr(1)	As(11)	As(12)	120.33 (4)	As(12)	As(13)	C(130)	98.8 (2)
Cr(1)	As(11)	Cl(11)	109.52 (7)	As(14)	As(13)	C(130)	107.1 (2)
Cr(1)	As(11)	C(110)	122.8 (3)	Cr(1)	As(14)	As(13)	121.64 (4)
As(12)	As(11)	Cl(11)	105.66 (7)	Cr(1)	As(14)	Cl(14)	108.36 (9)
C(142)	C(140)	C(143)	113.4 (7)	Cr(1)	As(14)	C(140)	121.4 (2)
C(111)	C(110)	C(113)	116.0 (9)	As(13)	As(14)	Cl(14)	105.74 (8)
C(112)	C(110)	C(113)	106.4 (9)	As(13)	As(14)	C(140)	99.5 (2)
As(12)	C(120)	C(121)	112.4 (5)	Cl(14)	As(14)	C(140)	96.5 (3)
As(12)	C(120)	C(122)	107.8 (6)	Cr(1)	C(11)	O(11)	175.3 (6)
As(12)	C(120)	C(123)	105.9 (7)	Cr(1)	C(12)	O(12)	177.8 (8)
C(121)	C(120)	C(122)	112.6 (9)	Cr(1)	C(13)	O(13)	175.8 (8)
C(121)	C(120)	C(123)	108.6 (9)	Cr(1)	C(14)	O(14)	176.7 (8)
C(122)	C(120)	C(123)	109.2 (8)	As(11)	C(110)	C(111)	106.4 (6)
As(13)	C(130)	C(131)	102.8 (5)	As(11)	C(110)	C(112)	110.9 (6)
As(13)	C(130)	C(132)	111.2 (5)	As(11)	C(110)	C(113)	106.3 (6)
As(13)	C(130)	C(133)	105.6 (5)				

lone pair donation through As atoms (see Scheme I). The actual mechanism of formation of this unusual product is at present unknown. The presence of Cl attached to As suggests an attack by Cl$^-$ on a coordinatively unsaturated and electron-deficient As atom.[20] Clearly, the oligomerization of a number of *t*-BuAs units has taken place. However, our data provide no real information on the mechanism and further speculation would be unwarranted at this stage.

X-ray Crystal Structure of (CO)$_4$CrAs-*t*-BuCl(As-*t*-Bu)$_2$As-*t*-BuCl (4). The complex crystallizes in the monoclinic space group $P2_1/n$ with two complete molecules per asymmetric unit (eight per unit cell). The structural parameters for each molecule are very similar. A view of one molecule is shown in Figure 3. Details of data collection, solution structure and refinement are given in Table I. Positional parameters for both molecules in the asymmetric unit, bond lengths, and bond angles for one molecule are presented in Tables V, VI, and VII, respectively. Each molecule has an idealized (not crystallographically imposed) two-fold axis running through the Cr atom and bisecting the As–As bond between the two As atoms not directly bound to Cr. The CrAs$_4$ ring is virtually planar.[21] The compound crystallizes as a racemate, each As bound to the Cr of each molecule is chiral. The two molecules of the asymmetric unit are the same isomer and each is related to its enantiomorphic isomer by the glide plane. The *tert*-butyl groups attached to adjacent As atoms adopt roughly trans positions with respect to each other, and this no doubt minimizes intramolecular steric repulsions. The bond lengths and angles for 4 fall within normal limits. Thus, the As–As distances of the ring in one molecule of 4, 2.478 (1), 2.427 (1), and 2.479 (1) Å, can be compared to the As–As single bond distances in (AsPh)$_6$ (average 2.459 Å).[22] The Cr–As distances (average value 2.42 Å) can be compared to the analogous Cr–As distances in [Cr(CO)$_4$]$_2$(AsMe$_2$)$_4$[23] (2.480 (1) Å and in Cr(CO)$_2$[(π-C$_6$H$_5$)(C$_6$H$_5$)As(CH$_2$)As(C$_6$H$_5$)$_2$] (2.406 (1) Å).[24] Further studies are in progress.

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Registry No. 3, 84133-62-0; 4, 88056-90-0; *t*-Bu$_2$AsCl, 4262-42-4; Na$_2$Cr$_2$(CO)$_{10}$, 15616-67-8.

Supplementary Material Available: Tables of general temperature factors and structure factors for 3 and complete tables of bond lengths, angles, temperature factors, and structure factors for 4 (78 pages). Ordering information is given on any current masthead page.

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[20] von Seyerl, J.; Sigwarth, B.; Huttner, G. *Chem. Ber.* **1981**, *114*, 727.

[21] Distance (Å) of atoms from least-squares plane: Cr(1), 0.021; As(11), 0.800; As(12), 1.256; As(13), −0.564; As (14) −1.613.

[22] See: Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327 for a brief review of As–As bond data.

[23] Cotton, F. A.; Webb, T. R. *Inorg. Chim. Acta* **1974**, *10*, 127.

[24] Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 1047.

[25] **Note Added in Proof**: See also Flynn et al. (Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460) for [Cr(CO)$_5$AsN(SiMe$_3$)]$_2$ and related complexes.