Table IV. ^{13}C NMR Chemical Shifts of BAL and DMSA Adducts (ppm)[a]

carbon atoms	TDA-BAL	PDA-BAL	BAL
CH_3	21.2		
CH_2	43.15	40.47	30.07
CH	59.5	58.83	45.56
CH_2OH	64.36	63.93	65.64
phenyl	130.0	129.2	
	131.5	130.6	
		132.0	

carbon atoms	TDA-DMSA	PDA-DMSA	DMSA[b]
CH_3	21.21		
CH	59.5	59.23	49.75
COOH	170.2	169.9	179.8
phenyl	130.2	129.31	
	131.6	130.1	
	139.7	131.3	
	140.4	142.9	

[a] Chemical shifts are downfield from Me_4Si. [b] Sample dissolved in H_2O at pH ~ 3.0.

Spectroscopy of DMSA Adducts. Although we were unable to grow single crystals of the DMSA adducts suitable for X-ray diffraction, there can be little doubt as to their identity. The infrared spectra of the adducts clearly show the OH groups of the acid as well as the C=O stretch of the acid. Also, the stretches due to substituted phenyl groups can be clearly seen. The mass spectra also show the presence of various recognizable fragments, although the parent ions are not observed, most likely due to facile CO_2 loss.

The NMR spectra are also informative. The ^{13}C NMR spectrum again displays the characteristic downfield shift of the resonances of the carbons attached to the sulfur atoms, upon coordination to arsenic. They shift from 49 to 59 ppm. The proton NMR spectrum is not straightforward. Since we are using only the meso form of DMSA, the proton NMR spectrum should only contain one singlet. However, we have had considerable difficulty observing this. It is impossible to completely remove all traces of water from the compounds, and it appears to cause some complexity in the spectrum. The aliphatic proton resonance is weak and broad, and this is probably due to exchange caused by the acid groups or water. In addition, other peaks appear sporadically, suggesting that there is some decomposition occurring in solution.

Summary

The ligating properties of several vicinal dithiols toward arylarsenic dichlorides was investigated. These compounds readily chelate to organoarsenic(III) compounds, forming stable five-membered rings with pyramidal arsenic. The arsenic shows no tendency to adopt higher coordination environments, preferring only three-coordination. The stable crystalline adducts can be isolated and their properties studied. The shift of the resonances of the carbons attached to the sulfurs in the ^{13}C NMR spectrum was found to be most indicative of coordination.

Supplementary Material Available: Tables of crystallographic data and anisotropic thermal parameters (2 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(20) Aksnes, D. W.; Vikane, O. *Acta Chem. Scand.* **1973**, *27*, 1337.

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Syntheses and Structures of K_3MQ_4 (M = Nb, Ta; Q = S, Se)

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The four tetrachalcogenometalates K_3NbS_4, K_3NbSe_4, K_3TaS_4, and K_3TaSe_4 have been obtained by direct reaction among the elements at 850 °C. The structures of K_3NbS_4 and K_3NbSe_4 have been determined by single-crystal X-ray diffraction methods. K_3TaS_4 and K_3TaSe_4 are isostructural with K_3NbS_4 and K_3NbSe_4, as determined from X-ray Guinier photographs. All of them crystallize with four formula units in space group D_{2h}^{16}-*Pnma* of the orthorhombic system in cells of dimensions $a = 9.214$ (8), $b = 10.484$ (6), and $c = 9.319$ (7) Å for K_3NbS_4, $a = 9.599$ (2), $b = 11.042$ (3), and $c = 9.660$ (2) Å for K_3NbSe_4, $a = 9.283$ (2), $b = 10.806$ (3), and $c = 9.387$ (2) Å for K_3TaS_4,and $a = 9.682$ (3), $b = 11.276$ (4), and $c = 9.712$ (3) Å for K_3TaSe_4. The final refinements of 43 variables lead to R and R_w values of 0.106 and 0.115 for K_3NbS_4 and 0.069 and 0.083 for K_3NbSe_4. These structures are of the K_3VS_4 type and contain discrete K^+ and tetrahedral MQ_4^{3-} ions. In K_3NbS_4 the Nb-S distances range from 2.241 (8) to 2.258 (8) Å and the S-Nb-S angles range from 108.3 (2) to 111.6 (3)°. In K_3NbSe_4 the Nb-Se distances range from 2.387 (1) to 2.403 (1) Å and Se-Nb-Se angles range from 108.49 (3) to 111.68 (5)°.

Introduction

Among the tetrachalcogenometalates MQ_4^{3-} (M = V, Nb, Ta; Q = S, Se, Te) only the VS_4^{3-} ion has been synthesized by wet-chemical methods.[1] Attempts to prepare MS_4^{3-} (M = Nb, Ta) from $M(OEt)_5$ and $S(SiMe_3)_2$ in acetonitrile led to the polynuclear cage anions $M_6S_{17}^{4-}$.[2] Similarly, a number of other synthetic strategies involving wet-chemical methods have failed to afford the $NbSe_4^{3-}$ or $TaSe_4^{3-}$ ions.[3] Hence, synthesis via solid-state reactions of the alkali-metal tetrachalcogenometalates A_3MQ_4 (M = Nb, Ta; Q = S, Se) and their subsequent dissolution might be a route to such ions. By direct combination of the constituent elements, some of these ions have been synthesized in the solid state. Thus Tl_3MQ_4[4] (M = V, Nb, Ta; Q = S, Se) and Cu_3MQ_4[5] (M = V, Nb, Ta; Q = S, Se, Te) have been obtained; these compounds adopt a cubic structure built from MQ_4^{3-} tetrahedra in which there are significant anion-cation interactions.

Table I. Crystal Data for K_3NbS_4 and K_3NbSe_4

formula	K_3NbS_4	K_3NbSe_4
fw	338.45	526.05
a, Å	9.214 (8)	9.599 (2)
b, Å	10.484 (6)	11.042 (3)
c, Å	9.319 (7)	9.660 (2)
V, Å^3	900.2	1023.8
Z	4	4
t, °C	-150	-150
d_{calcd}, g/cm^3	2.497	3.412
space group	D_{2h}^{16}-*Pnma*	D_{2h}^{16}-*Pnma*
μ, cm^{-1}	34.05	163.51
R on F_o	0.106	0.069
R_w on F_o	0.115	0.083

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(1) (a) Krüss, G.; Ohnmais, K. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2547-2552. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635-4642.

(2) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706-1713.

(3) Chau, C.-N. Unpublished results.

(4) Crevecoeur, C. *Acta Crystallogr.* **1964**, *17*, 757.

(5) Hulliger, F. *Helv. Phys. Acta* **1961**, *34*, 379-382.

0020-1669/90/1329-1503$02.50/0

Table II. Positional Parameters and B_{eq} (Å^2) for K_3NbS_4 and K_3NbSe_4

	site symmetry	K_3NbS_4				K_3NbSe_4			
		x	y	z	B_{eq}	x	y	z	B_{eq}
Nb	m	0.21274 (22)	$^3/_4$	0.51473 (24)	3.15 (7)	0.21235 (9)	$^3/_4$	0.51540 (9)	0.59 (1)
K(1)	1	0.05566 (38)	0.45556 (51)	0.28834 (42)	3.6 (1)	0.05567 (16)	0.45339 (14)	0.29262 (17)	1.06 (3)
K(2)	m	0.13557 (61)	$^3/_4$	0.07970 (70)	4.4 (2)	0.13112 (26)	$^3/_4$	0.08898 (27)	1.54 (5)
Q(1)	m	0.98943 (65)	$^3/_4$	0.41519 (69)	3.3 (2)	0.98315 (10)	$^3/_4$	0.41523 (11)	0.90 (2)
Q(2)	m	0.19154 (71)	$^3/_4$	0.75429 (79)	4.0 (2)	0.19123 (11)	$^3/_4$	0.76164 (11)	0.88 (2)
Q(3)	1	0.33272 (46)	0.57233 (63)	0.44883 (51)	3.8 (1)	0.33399 (8)	0.57095 (7)	0.44699 (9)	1.16 (1)

Table III. Selected Distances (Å) and Angles (deg) for K_3NbQ_4

	Q = S	Q = Se		Q = S	Q = Se
Nb–Q(1)	2.257 (8)	2.403 (1)	K(1)–Q(2)	3.161 (8)	3.307 (2)
Nb–Q(2)	2.241 (8)	2.387 (1)	K(1)–Q(2′)	3.189 (8)	3.322 (2)
Nb–Q(3)	2.251 (6)	2.389 (1)	K(1)–Q(3)	3.202 (8)	3.323 (2)
Nb–Q(3′)	2.251 (6)	2.389 (1)	K(1)–Q(3′)	3.256 (7)	3.401 (2)
Q(1)–Nb–Q(2)	109.3 (3)	108.87 (5)	K(1)–Q(3″)	3.340 (8)	3.513 (2)
Q(1)–Nb–Q(3)	109.6 (2)	109.63 (3)	K(2)–Q(1)	3.404 (10)	3.457 (3)
Q(1)–Nb–Q(3′)	109.6 (2)	109.63 (3)	K(2)–Q(1′)	3.261 (11)	3.379 (3)
Q(2)–Nb–Q(3)	108.3 (2)	108.49 (3)	K(2)–Q(2)	3.076 (10)	3.214 (3)
Q(2)–Nb–Q(3′)	108.3 (2)	108.49 (3)	K(2)–Q(3)	3.604 (7)	3.488 (2)
Q(3)–Nb–Q(3′)	111.6 (3)	111.68 (5)	K(2)–Q(3′)	3.366 (9)	3.488 (2)
K(1)–Q(1)	3.361 (6)	3.551 (2)	K(2)–Q(3″)	3.366 (9)	3.815 (2)
K(1)–Q(1′)	3.529 (8)	3.626 (2)	K(2)–Q(3‴)	3.604 (7)	3.815 (2)

The A_3MQ_4 compounds (A = alkali metal) also exist; the first to be described was K_3VS_4,[6] which crystallizes in space group *Pnma* of the orthorhombic system (a = 9.144 (4), b = 10.59 (1), c = 9.107 (4) Å). Recently, the synthesis of Cs_3NbSe_4 and Cs_3TaSe_4 and the structure (from neutron diffraction powder data) of Cs_3TaSe_4 were reported.[7] Here, we describe the syntheses and structures of K_3MQ_4 (M = Nb, Ta; Q = S, Se). The anion–cation interactions in these compounds are essentially ionic.

Experimental Section

Syntheses. Inside a glovebox under an Ar atmosphere 0.252 g of metallic K (Alfa 99%), 0.200 g of Nb powder (Aesar 99.8%), and 0.276 g of S powder (Mallinckrodt 99.93%) were placed in a silica tube that had been previously dried under vacuum. The tube was then sealed under vacuum (10^{-4} Torr) and heated in a furnace at 850 °C for 8 days. *Note: melting and sealing must be carried out very carefully in order to avoid ignition of metallic K with S, as that reaction is very exothermic.* The tube was cooled to 450 °C at 4 deg/h and then to room temperature at 20 deg/h. The product obtained was a red-pink powder; it contained some single crystals suitable for X-ray diffraction study. K_3NbSe_4 was prepared by the same route with the use of 0.680 g of Se powder (Aldrich 99.5%) instead of S. The product obtained was a brown-black powder together with some single crystals. The equivalent tantalum compounds (as powders) have been obtained by the same route with the use of Ta powder (Aldrich 99.9%) as a starting material. All these products are very air sensitive.

Analysis of these compounds with the microprobe of an EDAX-equipped Hitachi S570 scanning electron microscope indicated the presence of (K, Nb, S), (K, Nb, Se), (K, Ta, S), and (K, Ta, Se), respectively.

Structural Study. At the first stage of the structural investigation, the X-ray powder diffraction pattern of K_3NbS_4, obtained at room temperature on a Nonius FR552 Guinier camera, was indexed with the program TREOR[8] in an orthorhombic cell (a = 9.30, b = 10.76, c = 9.39 Å). The simulated X-ray diffraction pattern, generated by the program LAZY-PULVERIX[9] with atomic positions from the expected isostructural K_3VS_4 compound, shows very good agreement with the observed pattern. The observed X-ray powder pattern of K_3NbSe_4 is very similar to that of K_3NbS_4, and again the simulated pattern is in good agreement with the observed pattern. We conclude that the two compounds are isostructural.

The cell parameters for a single crystal of K_3NbS_4 were determined by a least-squares analysis of 25 reflections centered on a Picker FACS-1 diffractometer. Then, the intensities of 1343 unique reflections were recorded. The refined cell constants and additional crystal data are given in Table I. The cell parameters of K_3NbSe_4 have been obtained in a similar way; these and other crystal data are reported in Table I and in more detail in Table IS.[10]

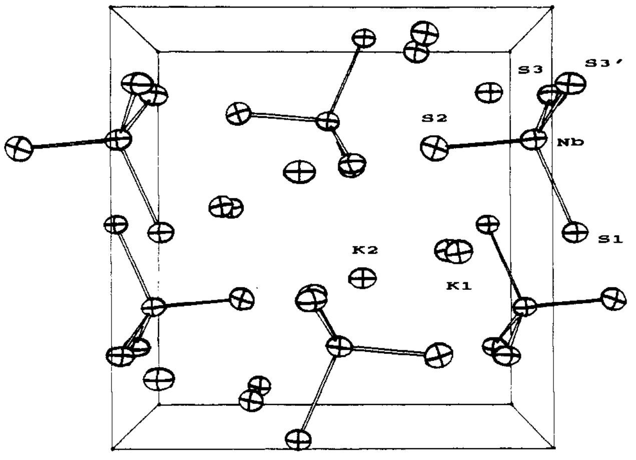

Figure 1. View of the unit cell of K_3NbS_4 along [010] with 50% probability ellipsoids.

All calculations were carried out on a Harris 1000 computer with programs and methods standard to this laboratory.[11] Conventional atomic scattering factors[12] were used, and anomalous dispersion corrections[13] were applied. An examination of the intensity data showed the systematic absences characteristic of space group *Pnma* or $Pn2_1a$. Space group *Pnma* was assumed, and initial positions for the Nb, K, and S atoms for K_3NbS_4 and Nb, K, and Se for K_3NbSe_4 were determined by the direct-methods program SHELX-86.[14] These positions were in good agreement with those of the corresponding atoms in K_3VS_4.[6] From a difference electron density synthesis we verified that all atoms had been located, and we then corrected the data for absorption.[15] The final cycles of refinement on F_o, which included anisotropic thermal parameters, resulted in final values of R and R_w of 0.106 and 0.115 for K_3NbS_4 and 0.069 and 0.083 for K_3NbSe_4. The final difference electron density maps for each compound contain no significant features compared to the height of a Nb atom. No unusual trends were found in an analysis of $|F_o|$ versus $|F_c|$ as a function of $|F_o|$, setting angles, and Miller indices. Final values

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(6) Van den Berg, J. M.; De Vries, R. *Proc. K. Ned. Akad. Wet.* **1964**, *B67*, 178–180.

(7) Yun, H.; Randall, C. R.; Ibers, J. A. *J. Solid State Chem.* **1988**, *76*, 109–114.

(8) Werner, P.-E. *Ark. Kemi* **1969**, *31*, 513–516.

(9) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73–74.

(10) Supplementary material.

(11) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(12) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K.; 1974; Vol. IV, Tables 2.2A, 2.3.1.

(13) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.

(14) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: London/New York, 1985; pp 175–189.

(15) De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

of the atomic parameters appear in Table II.

The cell parameters of powder samples of K_3TaS_4 and K_3TaSe_4 were each refined from 20 observations recorded at room temperature with an Enraf-Nonius FR552 Guinier camera ($\lambda(\mathrm{Cu}\ K\alpha_1) = 1.540562$ Å); Si SRM 640 ($a = 5.43088$ Å at 25 °C) was used as an internal standard. The cell constants are $a = 9.283$ (2), $b = 10.806$ (3), and $c = 9.387$ (2) Å for K_3TaS_4 and $a = 9.682$ (3), $b = 11.276$ (4), and $c = 9.712$ (3) Å for K_3TaSe_4.

Discussion

The structure of K_3NbS_4 is shown in Figure 1. It is built from the packing of NbS_4^{3-} anions and K^+ cations. Selected distances and angles are given in Table III. The Nb atom is tetrahedrally coordinated, and the range of Nb–S distances (from 2.241 (8) to 2.258 (8) Å) is near the sum of the ionic radii (2.32 Å).[16] The angles range from 108.3 (2) to 111.6 (3)° and are close to the tetrahedral value (109.47°). In K_3NbSe_4, the Nb–Se distances range from 2.387 (1) to 2.403 (1) Å and are also in fair agreement with the sum of the ionic radii (2.46 Å).[16] The Se–Nb–Se angles vary from 108.49 (3) to 111.68 (5)°. As expected, the metrical details of the $NbSe_4^{3-}$ ion are the same as those of the $TaSe_4^{3-}$ ion (Ta–Se = 2.369 (4)–2.397 (6) Å; Se–Ta–Se = 108.5 (2)–112.1 (2)°).[7]

The K–S geometries are not easily described in terms of classic polyhedra. If one takes a cutoff of 3.65 Å for the K–S distances, each K cation is surrounded by seven S atoms. The K–S distances range from 3.076 (10) to 3.604 (7) Å. Atom K(1) is linked to four different tetrahedra whereas atom K(2) is linked to five. A cutoff of 3.85 Å for the K–Se distances in K_3NbSe_4 leads to seven Se atoms about each K atom. The average value of 3.34 Å for the K–S distances and that of 3.48 Å for the K–Se distances are slightly longer than the sum of the ionic radii (3.30 and 3.44 Å, respectively). Similarly in Cs_3TaSe_4 the average Cs–Se distance is 3.71 Å compared with 3.70 Å for the sum of ionic radii. These compounds adopt orthorhombic symmetry and the interactions between the A cations and the Q atoms of the anions are essentially ionic, in accordance with the strong electronegativity difference ($\chi_S - \chi_K = 1.7$, $\chi_{Se} - \chi_K = 1.6$, and $\chi_{Se} - \chi_{Cs} = 1.7$). This is not true for Cu_3TaSe_4[5] and Tl_3TaSe_4[4] where the average A–Q distances are significantly shorter than the sums of ionic radii (Cu–Se = 2.41 Å versus 2.80 Å; Tl–Se = 3.22 Å versus 3.54 Å). If one considers the electronegativity differences ($\chi_{Se} - \chi_{Cu} = 0.5$ and $\chi_{Se} - \chi_{Tl} = 0.6$) between ions, then these interactions are much more covalent; this is evident in the shorter distances and perhaps in the more symmetric cubic structure. The weaker A–Q interactions observed in the alkali-metal tetrachalcogenometalates perhaps explain their solubility in nonaqueous solvents. The resultant solution chemistry is being investigated.

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Supplementary Material Available: Complete crystallographic details (Table IS), additional distances and angles (Table IIS), and anisotropic thermal parameters (Table IIIS) (4 pages); tables of observed and calculated structure amplitudes for K_3NbS_4 and K_3NbSe_4 (13 pages). Ordering information is given on any current masthead page.

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(16) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

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Preparation and Characterization of $(C_5Me_5)Rh(CNR)_2$ and $[(C_5Me_5)Rh(CNR)]_2$ Complexes

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Several complexes of the type $(C_5Me_5)M(CNR)X_2$ have been prepared, where M = Rh and Ir, X = Cl, Br, and I and R = Me, *t*-Bu, *neo*-Pn, *i*-Pr, 2,6-xylyl, and CH_2–adamantyl. Two members of this series have been structurally characterized. $(C_5Me_5)Rh(CNMe)Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.189$ (4) Å, $b = 8.442$ (2) Å, $c = 13.473$ (6) Å, $\beta = 111.31$ (6)°, $V = 1398$ (2) Å^3, and $Z = 4$. $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.364$ (3) Å, $b = 8.436$ (3) Å, $c = 22.015$ (9) Å, $\beta = 97.33$ (3)°, $V = 2093$ (2) Å^3, and $Z = 4$. Reduction of the dihalide derivatives in the presence of isocyanide provides a general route to the bis-substituted products $(C_5Me_5)Rh(CNR)_2$ (R = Me, *t*-Bu, *neo*-Pn, *i*-Pr, 2,6-xylyl, CH_2–adamantyl). Reduction of the dihalide complexes in the absence of added isocyanide gives the dimers $[(C_5Me_5)Rh(\mu\text{-}CNR)]_2$, one of which has been characterized by X-ray crystallography (R = 2,6-xylyl). The molecule was found to crystallize in the monoclinic space group $P2_1/a$ with $a = 11.165$ (6) Å, $b = 13.222$ (5) Å, $c = 11.228$ (8) Å, $\beta = 98.43$ (5)°, $V = 1639.6$ (2.9) Å^3, and $Z = 4$.

Introduction

A wide variety of complexes of the general formula $CpML_2$ and $(C_5Me_5)ML_2$, where M = Co, Rh, and Ir, have been prepared and isolated over the past 20 years.[1-3] Some of these low-valent group 8 metals have shown activity toward C–H bonds, and our interest in low-valent isocyanide complexes led to the investigation of the complexes $(C_5Me_5)M(CNR)_2$.[4] These species have been observed in substitution reactions of $(C_5Me_5)M(CO)_2$ in solution[5] and in ligand-substitution reactions of $(\mathrm{indenyl})Rh(C_2H_4)_2$.[6] Werner has recently reported the preparation of several $CpRh(CNR)_2$ complexes via $[RhCl(CNR)_2]_2$,[7] but a general preparation for the C_5Me_5 complexes has not appeared in the literature. In addition, while several μ-CO and μ-NO dimers of the type $[(C_5R_5)M(\mu\text{-}CO)_x(\mu\text{-}NO)_{2-x}]_2$ (R = H, Me; M = Co, Rh, Fe; $x = 0, 1, 2$) have been prepared[8] and structurally characterized,[9] only one isocyanide analogue has been reported, [CpNi-

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† A. P. Sloan Fellow, 1984–1986. Camille & Henry Dreyfus Teacher Scholar, 1985–1989.

(1) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301–307. Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1–48.

(2) King, R. B. *Inorg. Chem.* **1963**, *2*, 528–531. King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287–297.

(3) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927–949.

(4) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686–687.

(5) (a) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372–376. (b) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663.

(6) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648–649.

(7) Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* **1985**, *281*, 317–347.

(8) Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87–92. Shore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 255–256. Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21–C22. Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517–522. Müller, J.; Schmitt, S. *J. Organomet. Chem.* **1975**, *97*, C54–C56. Dimas, P. A.; Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1981**, *20*, 281–283. Shore, N. E. *J. Organomet. Chem.* **1979**, 173, 301–316. Brunner, H. *J. Organomet. Chem.* **1968**, *14*, 173–178.