Organometallics 1992, 11, 3353–3361

Synthesis and Electronic and Molecular Structures of η-Cycloheptatrienyl η-Cyclopentadienyl Derivatives of Vanadium, Niobium, and Tantalum: Photoelectron Spectroscopic, Electrochemical, and X-ray Crystallographic Study

Jennifer C. Green, Malcolm L. H. Green,* Nikolas Kaltsoyannis, Philip Mountford, and Peter Scott

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, United Kingdom

Stephen J. Simpson

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, United Kingdom

Received February 24, 1992

The new compounds $[Ta(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (3), $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)(thf)][PF_6]$ (R = H (4), Me (**4a**)), $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)(PMe_3)][PF_6]$ (5), $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)(CO)][PF_6]$ (6), $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_7H_7(\eta\text{-}C_5H_5)]$ (7), and $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)Me]$ (8) have been prepared, and an improved route to $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$ (R = H (2), Me (2a)) is reported. The X-ray crystal structures of **4a** and **7** have been determined. The He I and He II photoelectron spectra of $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (M = V, Nb) and **3** have been obtained and the bonding is discussed. It is considered that $(\eta\text{-}C_7H_7)$–M bonding requires a contribution of three valence electrons from the metal.

A substantial chemistry of $(\eta\text{-}C_7H_7)$–M derivatives of the groups 4–6 metals (except Ta) is known. However, the nature of the $(\eta\text{-}C_7H_7)$–M bond is not understood in detail. Indeed, the formal oxidation state of the η-cycloheptatrienyl ligand in its complexes is open to debate,[1] as both a +1 and a −3 formal charge satisfy the Hückel $4n + 2$ rule for aromaticity. In this paper we attempt to identify more closely the functional group properties of the η-cycloheptatrienyl ligand by examining the photoelectron (PE) spectroscopic and electrochemical properties of some of its complexes with the group 5 transition metals. Sandwich compounds are particularly well suited to this, since they give rise to PE spectra with well-separated bands of metal, ligand, and mixed metal/ligand character and normally undergo clean electron-transfer processes.[2] We have chosen in the main part to study complexes of the general class $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$. Part of this work has been communicated.[3]

Results and Discussion

Synthetic Studies. $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (M = V[4] (**1**), Nb[5] (**2**)) have long been known, and we have recently described new syntheses of **2** and $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (**2a**).[6] We have found improved syntheses for **2** and **2a**, and a route to the first η-cycloheptatrienyl complex of tantalum, namely $[Ta(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (**3**), is described below.

Reduction of $[Nb(\eta\text{-}C_5H_5)Cl_4]$ with magnesium in thf in the presence of an excess of cycloheptatriene gives, after extraction, sublimation, and crystallization, a 40% yield of maroon **2** (scale ca. 3 g), which was identified by comparison of the mass and IR spectra with the original reports.[5] Analytical and spectroscopic data for **2** and all of the other compounds described in this work are collected in Table I. Similarly, a solution of $[Nb(\eta\text{-}C_5H_4Me)Cl_4]$ in thf and cycloheptatriene was stirred over magnesium turnings to give a red-brown solution from which petroleum ether soluble crystals of **2a** were isolated in 43% yield. The ESR spectrum of **2a** at 293 K in toluene showed a decet ($A[Nb]_{iso} = 34.0$ G, $g_{iso} = 1.986$) although, as with **2** no proton hyperfine coupling could be resolved.[5]

A solution of $[Ta(\eta\text{-}C_5H_4Me)Cl_4]$ and cycloheptatriene in thf was cooled to −80 °C and was transferred onto magnesium turnings. The stirred mixture changed from yellow through green and red to brown over a period of 3 h. Crystallization from petroleum ether and sublimation gave an amorphous solid. Crystallization of the sublimate from petroleum ether gave highly-sensitive, purple-blue crystals of **3** in 12% yield. The ESR spectrum in toluene at 293 K showed a broad isotropic octet from coupling to tantalum (spin $I = {}^7/_2$) ($A[Ta]_{iso} = 71.6$ G, $g_{iso} = 1.951$). No proton hyperfine splitting was resolved. A frozen toluene solution at 92 K showed parallel and perpendicular features with g(parallel) = 1.991, g(perpendicular) = 1.921, A(Ta)(parallel) = 166.8 G and A(Ta)(perpendicular) < 7 G. No proton hyperfine structure was resolved. We were unable to isolate the unsubstituted cyclopentadienyl analogue $[Ta(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$.

Electronic Structures of the Compounds $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$. The bonding in mixed sandwich molecules has been the subject of a number of both theoretical and experimental investigations,[1,7–13] but only those aspects

---

(1) Davies, C. E.; Gardiner, I. M.; Green, J. C.; Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 669.

(2) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* *23*, 1.

(3) Green, M. L. H.; Mountford, P.; Mtetwa, V. S. B.; Simpson, S.; Scott, P. *J. Chem. Soc., Chem. Commun.* **1992**, *314*.

(4) King, R. B. *Organomet. Synth.* **1965**, *1*, 140.

(5) Van Oven, H. C.; Groenenboom, C. J.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 379.

(6) (a) Green, M. L. H.; Mounford, P.; Mtetwa, V. S. B.; Scott, P. *Polyhedron* **1991**, *10*, 389. (b) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Simpson, S.; Scott, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1591.

(7) Evans, S.; Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1974**, 304.

(8) Groenenboom, C. J.; Sawatsky, G.; De Liefde Meijer, H. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *76*, C4.

(9) Groenenboom, C. J.; De Liefde Meijer, H. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *69*, 235.

(10) Groenenboom, C. J.; De Liefde Meijer, H. J.; Jellinek, F.; Oksam, A. *J. Organomet. Chem.* **1975**, *97*, 73.

(11) Warren, K. D. *Struct. Bonding* **1976**, *27*, 45 and references therein.

(12) Clack, D. W.; Warren, K. D. *J. Organomet. Chem.* **1978**, *152*, C60.

(13) Cloke, F. G. N.; Dix, A.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150.

0276-7333/92/2311-3353$03.00/0

Table I. Analytical and Spectroscopic Data for [Nb(η-C_7H_7)(η-C_5H_4Me)] (2a), [Ta(η-C_7H_7)(η-C_5H_4Me)] (3), [Nb(η-C_7H_7)(η-C_5H_5)(thf)][PF_6] (4), [Nb(η-C_7H_7)(η-C_5H_4Me)(thf)][PF_6] (4a), [Nb(η-C_7H_7)(η-C_5H_4Me)(PMe_3)][PF_6] (5), [Nb(η-C_7H_7)(η-C_5H_4Me)(CO)][PF_6] (6), [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (7), and [Nb(η-C_7H_7)(η-C_5H_4Me)Me] (8)

compd	color	C[a]	H[a]	spectroscopic data[b,c]
2a	maroon	58.8 (59.3)	5.4 (5.4)	selected IR: 1499 (w), 1133 (br), 1038 (m), 1026 (m), 949 (m), 849 (m), 781 (s) mass spectrum: $m/z = 263$ (M^+), 91 (C_7H_7) ESR (toluene, 293 K): decet, $A[\mathrm{Nb}]_{\mathrm{iso}} = 34.0$ G, $g_{\mathrm{iso}} = 1.986$
3	blue	44.3 (44.5)	3.9 (4.0)	selected IR: 1306 (m), 1262 (m), 1153 (br), 1084 (br), 1025 (s), 949 (m), 848 (m), 780 (s), 467 (w) mass spectrum: $m/z = 351$ (M^+), 338 (M – CH), 323 (M – C_2H_4), 91 (C_7H_7) ESR (toluene, 293 K): octet, $A[\mathrm{Ta}]_{\mathrm{iso}} = 71.6$ G, $g_{\mathrm{iso}} = 1.951$
4	red	41.1 (41.2)	4.3 (4.3)	^1H NMR (dichloromethane-d_2): 5.60 (s, 5 H, η-C_5H_5), 5.57 (s, 7 H, η-C_7H_7), 3.92 (br s, 4 H, OCH_2), 2.00 (br m, 4 H, OCH_2CH_2)
4a	red	42.3 (42.5)	4.5 (4.6)	^1H NMR (dichloromethane-d_2): 5.45 [vt, 2 H, C(Me)C*H* or C(Me)CHC*H*], 5.40 (s, 7 H, η-C_7H_7), 5.33 [vt, 2 H, C(Me)C*H* or C(Me)CHC*H*], 3.66 (br m, 4 H, OCH_2), 2.26 (s, 3 H, CH_3), 1.91 (m, 4 H, OCH_2CH_2) ^{13}C NMR (dichloromethane-d_2): 117.8 (s, CCH_3), 102.5 [d, *J*(CH) 175, C(Me)*C*H or C(Me)CH*C*H], 100.8 [d, *J*(CH) 175, C(Me)*C*H or C(Me)CH*C*H], 89.0 [d, *J*(CH) 175, η-C_7H_7], 75.7 [t, *J*(CH) 139, OCH_2], 26.3 [t, *J*(CH) 135, OCH_2CH_2], 15.5 [q, *J*(CH) 129, CH_3]
5	yellow	39.6 (39.7)	4.8 (4.8)	^1H NMR (dichloromethane-d_2): 5.21 [d, 4 H, *J*(PH) 6, C(Me)C*H* and C(Me)CHC*H*], 5.10 [d, 7 H, *J*(PH) 6, η-C_7H_7], 2.21 (s, 3 H, η-$C_5H_4CH_3$), 1.47 [d, 9 H, *J*(PH) 8, PMe_3] ^{13}C NMR (dichloromethane-d_2): 116.8 (s, CCH_3), 102.2 [d, *J*(CH) 176, C(Me)*C*H or C(Me)CH*C*H], 96.7 [d, *J*(CH) 178, C(Me)*C*H or C(Me)CH*C*H], 88.4 [d, *J*(CH) 171, η-C_7H_7], 20.2 [q of d, *J*(CH) 137, *J*(PC) 22, PMe_3], 17.3 [q, *J*(CH) 128, η-$C_5H_4CH_3$] ^{31}P NMR (dichloromethane-d_2): 6.5 (s, PMe_3), –146.7 (septet, PF_6^-)
6				^1H NMR (dichloromethane-d_2): 5.73 (s, 5 H, η-C_5H_5), 5.52 (s, 7 H, η-C_7H_7) IR: 2086 (vs)
7	blue	52.0 (52.2)	6.5 (6.6)	
8	red-brown	60.2 (60.4)	5.9 (6.2)	^1H NMR (benzene-d_6): 4.72 [s, 2 H, C(Me)C*H* or C(Me)CHC*H*], 4.46 [overlapping s, 9 H, η-C_7H_7 and (C(Me)C*H* or C(Me)CHC*H*)], 1.73 (s, 3 H, CCH_3), 0.11 (s, 3 H, $NbCH_3$) $^{13}C\{^1H\}$ DEPT NMR (benzene-d_6): 100.1 [C(Me)*C*H or C(Me)CH*C*H], 96.1 [C(Me)*C*H or C(Me)CH*C*H], 86.3 (η-C_7H_7), 14.9 (CCH_3)

[a] Given as % found (% calculated). [b] IR spectra obtained as Nujol mulls. IR abbreviations: vs = very strong, s = strong, m = medium, w = weak, br = broad. [c] NMR data given as chemical shift (δ) [multiplicity, *J*(Hz), relative intensity, assignment]. Chemical shifts are referenced internally using residual protio solvent resonances (^1H and ^{13}C) relative to tetramethylsilane (δ = 0 ppm) or externally using trimethyl phosphate in D_2O (^{31}P). NMR abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, vt = virtual triplet, br = broad, *J* = coupling constant in hertz, DEPT = distortionless enhancement by polarization transfer.

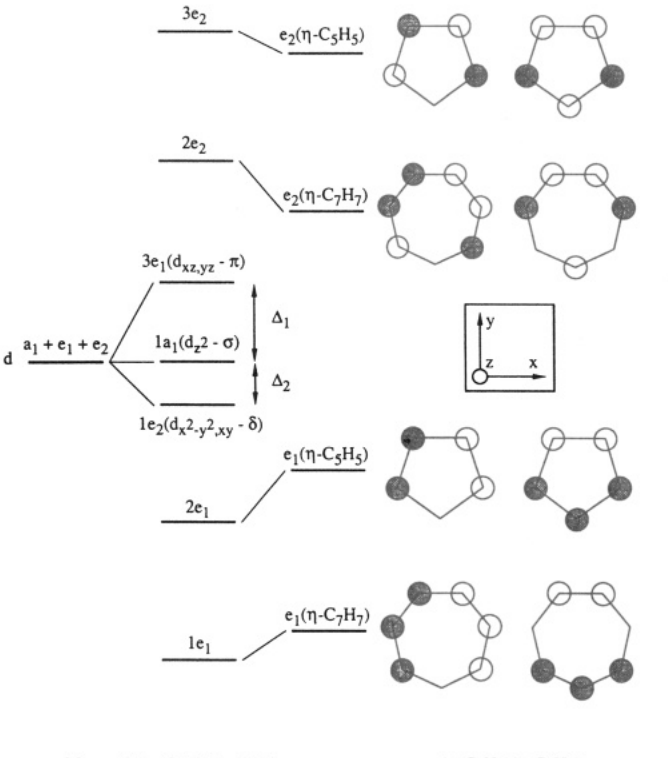


Figure 1. Qualitative molecular orbital diagram for [M(η-C_7H_7)(η-C_5H_5)], with symmetry labels appropriate to the $C_{\infty v}$ point group. Shadings indicate the phases of the carbon $2p_z$ atomic orbitals.

directly relevant to this work will be considered here. The previously-described X-ray crystal structures of [Ti(η-C_7H_7)(η-C_5H_5)],[14] [V(η-C_7H_7)(η-C_5H_5)],[15] and [Cr(η-C_7H_7)(η-C_5H_5)][16] show that the two hydrocarbon rings are planar and parallel, and it may be reasonably assumed that the analogous **2** and **3** have similar structures. The molecules may be assigned in the $C_{\infty v}$ point group, and a qualitative molecular orbital (MO) diagram is given in Figure 1 (in which only the e symmetry pπ orbitals of the ligands are considered). The metal d orbitals split into three sets;[17] d_{z^2} ($1a_1$), d_{xz}, d_{yz} ($3e_1$) and $d_{x^2-y^2}$, d_{xy} ($1e_2$), which are of σ, π, and δ symmetry with respect to the metal–ring centroid axes. In [M(η-C_7H_7)(η-C_5H_4R)] (M = V, Nb, and Ta), the $1a_1$ orbital is the HOMO and is occupied by one electron.

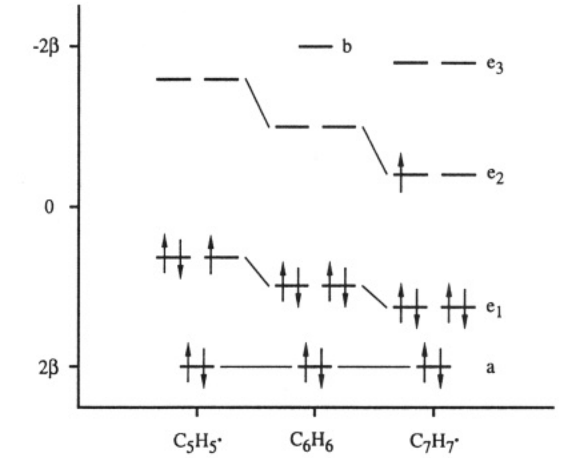


Figure 2. Hückel energies of the π orbitals of $C_5H_5^{\bullet}$, C_6H_6, and $C_7H_7^{\bullet}$.

Figure 2 shows the relative energies of the pπ MOs in cyclic C_nH_n (n = 5–7) systems, calculated using the Hückel

---

[14] Zeinstra, J. D.; de Boer, J. L. *J. Organomet. Chem.* **1973**, *54*, 207.

[15] Engebreston, G.; Rundle, K. E. *J. Am. Chem. soc.* **1963**, *85*, 481.

[16] Russell, R. D. cited in ref 9.

[17] Clack, D. W.; Warren, K. D. *Theor. Chim. Acta* **1977**, *46*, 313.

Table II. Vertical Ionization Energies and Assignments of [V(η-C_7H_7)(η-C_5H_5)] (1), [Nb(η-C_7H_7)(η-C_5H_5)] (2), and [Ta(η-C_7H_7)(η-C_5H_4Me)] (3)

compd	band	IE/eV	assgn
1[a]	A	6.49 (6.42)	$^1A_1$ ($1a_1$)
	B	6.86 (6.77)	$^3E_2$ ($1e_2$)
	B′	7.35 (7.28)	$^1E_2$ ($1e_2$)
	C	8.72 (8.66)	$2e_1$ (cp)
	C′	9.04 (8.99)	$2e_1$ (cp)
	D	10.40 (10.20)	$1e_1$ (cht)
2[b]	A	5.85 (5.98)	$^1A_1$ ($1a_1$)
	B	7.00 (7.11)	$^3E_2$ ($1e_2$)
	B′	7.36 (7.50)	$^1E_2$ ($1e_2$)
	C	8.77 (8.78)	$2e_1$ (cp)
	C′	9.23 (9.13)	$2e_1$ (cp)
	D	10.22 (10.4)	$1e_1$ (cht)
		11.44	ligand σ and π
		12.72	
3	A	5.47	$^1A_1$ ($1a_1$)
	B	6.89	$^3E_2$ ($1e_2$)
	B′	7.21	$^1E_2$ ($1e_2$)
	C	8.73	$2e_1$ (cp)
	C′	9.14	$2e_1$ (cp)
	D	10.19	$1e_1$ (cht)
		11.80	ligand σ and π
		12.65	
		14.62	
		16.17	

[a] Data in parentheses from ref 7. [b] Data in parentheses from ref 10.

Table III. Relative Band Intensities in the He I and He II Spectra of [V(η-C_7H_7)(η-C_5H_5)] (1), [Nb(η-C_7H_7)(η-C_5H_5)] (2), and [Ta(η-C_7H_7)(η-C_5H_4Me)] (3)

	$1a_1$	$1e_2$	$2e_1$ (η-C_5H_5)	$1e_1$ (η-C_7H_7)
	Compound 1			
He I	0.027	0.259	0.305	0.415
He II	0.045	0.308	0.323	0.324
He II/He I ($R_{II/I}$)	1.67	1.19	1.06	0.78
	Compound 2			
He I	0.063	0.318	0.341	0.278
He II	0.105	0.408	0.247	0.240
He II/He I ($R_{II/I}$)	1.67	1.28	0.72	0.86
	Compound 3			
He I	0.062	0.349	0.335	0.253
He II	0.095	0.381	0.283	0.240
He II/He I ($R_{II/I}$)	1.52	1.09	0.84	0.95

approach.[18] It can be seen that the ring e MOs become progressively stabilized with increasing ring size. The relative energies of these ligand e orbitals and the metal d orbitals are such that the main contribution to metal-ligand bonding for cyclopentadienyl rings is from the π MOs (e_1). However, for the cycloheptatrienyl ring, the δ MOs (e_2) are more important.

In the [M(η-C_7H_7)(η-C_5H_5)] compounds, the $1a_1$ orbital is essentially nonbonding (as the nodal cone of the d_{z^2} orbital intersects the metal-directed lobes of the p_z orbitals of the rings close to their region of maximum electron density). The Ta ESR data provide evidence for the high d_{z^2} character. An analysis of the data, comparable with that carried out for the group V bis(arene) compounds,[13] indicates a *d*/*s* ratio of 10 to 1 evidenced by the large difference in the *A*(parallel) and *A*(perpendicular) values. The $3e_1$ orbitals are strongly antibonding and the $1e_2$ orbitals metal → carbon back-bonding in nature. The a_1–e_1 (Δ_1) (Figure 1) separation is greater than that of a_1–e_2 (Δ_2).

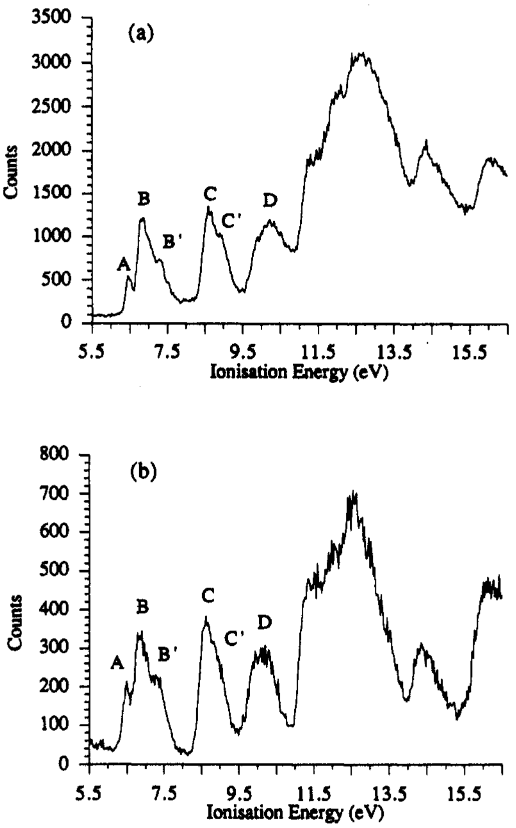


Figure 3. (a) He I and (b) He II photoelectron spectra of [V(η-C_7H_7)(η-C_5H_5)].

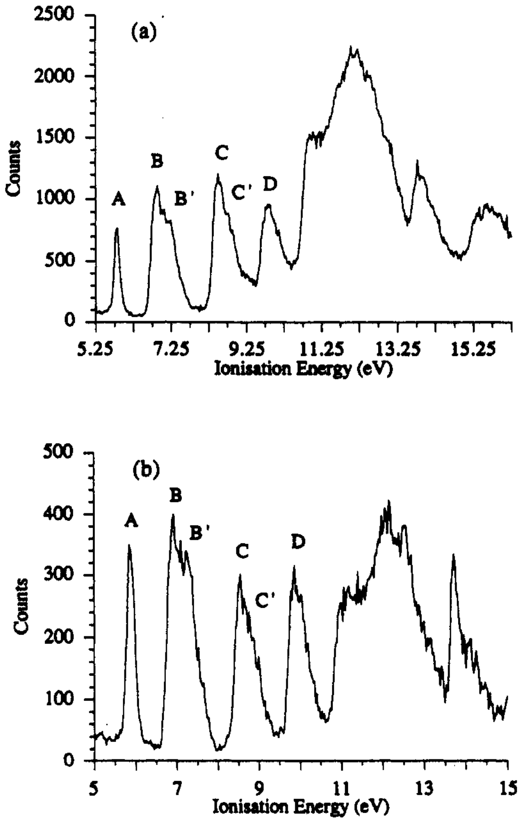


Figure 4. (a) He I and (b) He II photoelectron spectra of [Nb(η-C_7H_7)(η-C_5H_5)].

Symmetry permits mixing of both ring e_1 levels with the metal e_1 orbitals and with each other. On energy grounds we expect the (η-C_7H_7) e_1 orbitals to be the principal contributors to the $1e_1$ complex MOs, and the (η-C_5H_5) e_1

---

[18] Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; Wiley-Interscience: New York, 1991.

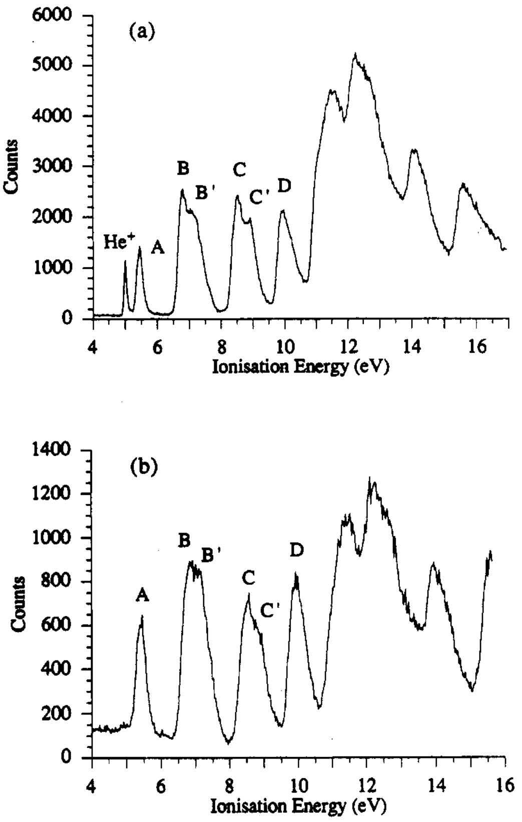


Figure 5. (a) He I and (b) He II photoelectron spectra of [Ta(η-C_7H_7)(η-C_5H_4Me)].

levels to be the main contributors to the $2e_1$.

The He I and He II PE spectra of **1**–**3** are presented in Figures 3–5. Vertical ionization energy (IE) data and assignments are given in Table II. The He I spectra of **1** and **2** have been reported previously, and the IE data are those obtained in this study while those in parentheses refer to the previous work.[7,10] Table III presents the relative areas of the four bands in the spectra of **1**–**3**, together with their $R_{II/I}$ values, i.e. the relative areas in the He II spectra divided by those in the He I.

The assignments put forward in Table II are as given by previous workers.[1,7,10] Above ca. 11 eV are found ionizations corresponding to the lowest-lying π orbitals and σ orbitals of the ligands. Below 11 eV four bands are observed, two of which (bands B and C) have distinct structure. The first band, A, is sharp and is assigned to ionization from the $1a_1$ MO, which is mainly metal d_{z^2} in character. Band B is assigned to ionization from the metal–cycloheptatrienyl δ bonding $1e_2$ MOs, the splitting of which arises from the $^3E_2$ and $^1E_2$ molecular ion states that are generated upon ionization of these 17 valence-electron compounds. The separation of the $^3E_2$ and $^1E_2$ ion states decreases as the group is descended, from 0.49 eV in **1** to 0.36 eV in **2** and 0.32 eV in **3**. This is as expected for a splitting arising from an exchange interaction and is found in the PE spectra of the bis(arene) compounds [M(η-C_6H_5R)$_2$] (M = V, Nb; R = H, Me)[13] (no PE data exists for bis(arene)tantalum). The first band in the spectrum of **3** arises from the ionization of helium atoms by He II radiation.

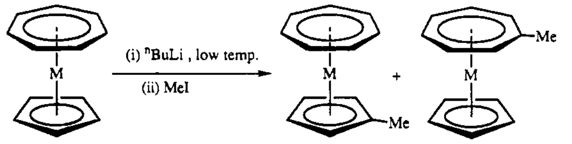
Bands C and D arise from ionization of the $2e_1$ (mainly cyclopentadienyl) and $1e_1$ (mainly cycloheptatrienyl) levels, respectively, MOs which have substantially less metal d character than the $1a_1$ and $1e_2$. The asymmetry of band C, which is more pronounced in the spectrum of **3**, probably arises from a Jahn–Teller distortion localized on the cyclopentadienyl ring.

The degree of interaction of the metal e_2 ($d_{x^2-y^2}$, d_{xy}) and ligand e_2 (cycloheptatrienyl) orbitals is of great importance in the description of the nature of the (η-C_7H_7)–transition metal bond and has been addressed a number of times using both spectroscopic and chemical evidence.[1,7-13]

The relative intensities of bands in ultraviolet PE spectra have been used to assess the localization properties of MOs,[19,20] based on the fact that the ionization cross section of metal d electrons increases relative to carbon 2p electrons as the photon energy is increased from He I (21.22 eV) to He II (40.81 eV). Consequently, PE bands with significant metal d character gain in intensity with respect to ligand-based ionizations as the incident photon energy is increased.

The $R_{II/I}$ values in Table III confirm that the $1a_1$ MO is a largely metal-based orbital. In both **2** and **3** the $2e_1$ (mainly cyclopentadienyl) MOs appear to have the least metal character, supporting the view that the structure of band C is not due to singlet–triplet splitting. In **1**, however, it is the $1e_1$ MOs which have the least metal character, indicating a switch of d character from the $2e_1 \rightarrow 1e_1$ MOs as the group is descended. In all three cases, the $R_{II/I}$ value of the $1e_2$ ionization bands is intermediate between that of the $1a_1$ and the $1e_1$ and $2e_1$. This implies that there is a significant contribution from both ligand and metal valence orbitals to the (η-C_7H_7)–M bonding MOs. On the basis of these values we tentatively suggest that the metal d orbital character of the $1e_2$ MOs decreases in the order Nb > V > Ta.

Groenenboom et al. have performed a series of methylation reactions by the sequence shown in eq 1.[9] It was



(1)

found that methylation occurs preferentially at the C_7 ring for M = Ti and at the C_5 ring for M = V and Cr. Also, the rate of metalation increases in the sequence Cr < V < Ti (most reactive). This was taken to indicate that "the negative charge on the carbon atoms of the seven-membered ring increases in the same sequence". We, however, would prefer to come to the opposite conclusion since one would expect that the nucleophilic *n*-butyl anion would attack the most *positive* (most electrophilic) ring. In other words, the most positively charged ring would have the most acidic C–H bonds. This is a *kinetic* argument in that it concerns the initial site of nucleophilic attack or deprotonation. However, inter-ring proton migration may occur at this point, leading to different products. Indeed, Elschenbroich has proposed a similar hydrogen-transfer process.[21] It is possible then that the initial site of presumed lithiation of [M(η-C_7H_7)(η-C_5H_5)] is not the same as that of the eventual methylation. Hence these experiments do not allow us to assign confidently the relative localization of charge on the carbocyclic rings of [M(η-C_7H_7)(η-C_5H_5)] systems.

Comparison of the IE data obtained for these group 5 complexes reveals that the $1e_1$ (cycloheptatrienyl) levels are effectively insensitive to changes in the metal. The $2e_1$ (cyclopentadienyl) and $1e_2$ MOs also show little change as the group is descended. The 0.05-eV increase in IE of

---

[19] Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

[20] Green, J. C. *Struct. Bonding* **1981**, *43*, 37.

[21] Elschenbroich, Ch.; Gerson, F.; Heinzer, J. *Z. Naturforsch. B* **1972**, *27B*, 312.

Table IV. Ligand Field Analysis of Some Group 5 Metal Sandwich Cations

cation	Δ_2/eV	B/eV	β[a]
$[V(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^+$	1.72	0.031	0.43
$[Nb(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^+$	2.14	0.023	0.42
$[Ta(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)]^+$	2.47	0.024	0.40
$[V(\eta\text{-}C_6H_6)_2]^{+}$[b]	1.91	0.047	0.63
$[V(\eta\text{-}C_6H_5Me)_2]^{+}$[b]	1.87	0.046	0.63
$[V(\eta\text{-}C_6H_3Me_3)_2]^{+}$[b]	1.78	0.047	0.64
$[Nb(\eta\text{-}C_6H_6)_2]^{+}$[b]	2.14	0.031	0.57
$[Nb(\eta\text{-}C_6H_5Me)_2]^{+}$[b]	2.01	0.035	0.57
$[Nb(\eta\text{-}C_6H_3Me_3)_2]^{+}$[b]	1.95	0.035	0.66

[a] Values for $B_{\text{free ion}}$ from ref 22. [b] Data from ref 13.

the $2e_1$ (cyclopentadienyl) MOs as the metal is changed from V to Nb, attributed to a greater metal–$e_1(\pi)$ interaction in Nb than in V,[10] is not continued in the third row compound, probably as a result of the methylation of the five-membered ring. This may also account for the similar trend observed in the $1e_2$ IEs.

The most significant effect of altering the metal atom occurs in the $1a_1$ MO, the IE of which drops 0.57 eV from 1 to 2 and by a further 0.38 eV from 2 to 3. This orbital, which the evidence suggests is almost purely metal d_{z^2}, reflects most closely the energy of the metal d electrons in the complex. The gap between the a_1 and the e_2 ionizations consequently increases down the group, from 0.35 eV for 1 ($^3E_2$–$^1A_1$) to 1.15 eV for 2 and 1.42 eV for 3. Ligand field parameters may be established for metal sandwich compounds using the expressions given below,[11,13] in which A, B, and C are the usual Racah parameters for measuring interelectronic repulsions. For d^4 cations

$$E(^1A_1) = 6A + 24B + 8C$$
$$E(^3E_2) = 6A - 8B + 5C + \Delta_2$$
$$E(^1E_2) = 6A + 7C + \Delta_2$$

from which it follows that

$$^3E_2 - {}^1A_1 = \Delta_2 - 44B \quad \text{and} \quad {}^1E_2 - {}^3E_2 = 16B$$

by assuming that $C = 4B$. Using the information obtained from the PE spectra, values for Δ_2, B, and β (the nephelauxetic ratio) have been calculated, and these are given in Table IV, together with corresponding data for bis(arene) compounds of V and Nb. Similar data for both 1 and 2 have been presented earlier,[11] based upon the original PE studies of these compounds. It should be noted, however, that the above derivations neglect spin–orbit coupling. This will be small for complexes of the first and second row metals but may be significant for third row elements. The e_2 levels of 3 may be split not only by singlet–triplet interaction, but also by spin–orbit coupling. In free Ta^+, the splitting of the $5d_{3/2}$ and $5d_{5/2}$ levels is predicted as $2\zeta = 0.44$ eV,[22] although delocalization of the metal d electrons onto the cycloheptatrienyl ring will reduce the magnitude of any splitting of the e_2 MOs. The $R_{II/I}$ data suggest that the metal d orbital character of the e_2 levels is smallest in 3, and hence it is unlikely that spin–orbit coupling plays any significant role in the asymmetry of band B. Furthermore, a spin–orbit splitting of the e_2 band should give rise to a 1:1 splitting. The relative areas of the components of band B are very close to the 3:1 ratio expected from a spin–spin interaction.

As expected, there is a significant drop in the electron–electron repulsion parameter B on moving from V to Nb and Ta, as is also observed for the bis(arene) compounds

Table V. Solution Electrochemical and Gas-Phase Ionization Energy Data for Some $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$ (M = V, Nb, Ta) Systems

compd	$E_{1/2}$-(red)/V[a]	$E_{1/2}$-(ox)/V[b]	first IE/eV
$[V(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (1)		+0.19	6.42
$[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (2)	−2.40	−0.82	5.85
$[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (2a)	−2.40	−0.82	
$[Ta(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4Me)]$ (3)		−1.18	5.47

[a] In thf/0.1 M TBAH. [b] In acetonitrile/0.1 M TBAH.

$[M(\eta\text{-}C_6H_6)_2]$ (M = V and Nb),[13] reinforcing further the view that an exchange interaction is the cause of the splitting of band B. The reduced B and β values obtained for the mixed ring species are in accordance with the expectation of a stronger metal–ligand interaction through the δ orbitals of the cycloheptatrienyl ring, supporting the assertion that there is a significant contribution from both metal and ligand orbitals in these MOs. In addition, the ligand field splitting parameter, Δ_2, increases steadily as the group is descended, as is expected for second and third vs first row metals.

Cyclic Voltammetry Studies on $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$. Since sandwich compounds almost invariably undergo electron-transfer reactions,[2] it was of interest to investigate the possibility of synthesizing both their oxidized and reduced forms. It was found that both 2 and 2a undergo fully reversible oxidation at −0.82 V vs the SCE in acetonitrile/0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH). The potentials were referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple at +0.355 V relative to the SCE, and the reversibility was judged by comparison of ΔE_P at various scan rates with that of the Fc^+/Fc internal standard.[23] Electrochemical data for this and other systems studied are summarized in Table V, together with gas-phase first IEs obtained by PE spectroscopy. In contrast, 2 and 2a are rather less well behaved in reduction. In acetonitrile, a broad irreversible wave was found at $E_{P_a} = -2.49$ V for 2, which showed a small reverse wave when the cell was cooled to −25 °C. The width of irreversible waves is diagnostic of electron-transfer behavior[24] in that irreversible but Nernstian 1-electron systems have $(E_P - E_{P/2}) \approx 60$ mV (where $E_{P/2}$ is the potential at half peak height).[25] Here, however, it was found that $(E_P - E_{P/2}) \approx 100$ mV at 100 mV s^{-1}. Also, the appearance of a small reverse wave on lowering the temperature indicates that the rate of some homogeneous reaction had been slowed. Presumably then, reduction of 2 to 2^- is followed by some fairly rapid decomposition reaction, possibly involving the solvent (acetonitrile).

The reduction wave of 2 in thf, however, appeared to be quasi-reversible ($\Delta E = 180$ mV at 100 mV s^{-1}); i.e. the system is still under charge-transfer and diffusion control, but it is at least chemically reversible. Attempts to make a more complete study of the cyclic voltammetry (CV) characteristics of the $2/2^-$ couple were precluded by the proximity of the waves to the solvent discharge. Nonetheless, this couple is chemically reversible in dry thf, and it should therefore be possible to reduce both 2 and 2a using potassium ($E^\circ = -2.942$ V for K^+/K versus the NHE).

CV studies on 3 were less conclusive. A slightly broad but chemically reversible couple ($\Delta E_P = 100$ mV at $\nu = 200$ mV s^{-1}) was detected at $E_{1/2} = -1.175$ V. Repeated scan-

---

(22) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1964.

(23) Koepp, H. M.; Wendt, H.; Stehlow, H. *Z. Electrochem.* **1960**, *64*, 483.

(24) Maloy, J. T. *J. Chem. Educ.* **1983**, *60*, 285.

(25) Pufahl, D.; Geiger, W. E. *Organometallics* **1989**, *8*, 412.

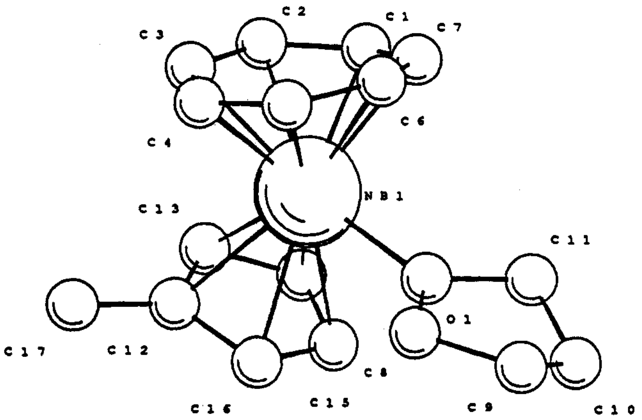


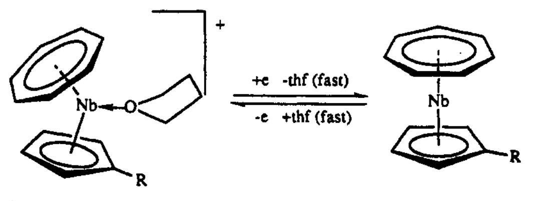
Figure 6. Cation molecular structure of [Nb(η-C_7H_7)(η-C_5H_4Me)(thf)][PF_6] (**4a**). (Hydrogen atoms ar omitted for clarity.) Selected bond lengths (Å): Nb(1)–C(1) 2.281 (5); Nb(1)–C(2) 2.331 (5); Nb(1)–C(3) 2.232 (6); Nb(1)–C(4) 2.273 (5); Nb(1)–C(5) 2.340 (6); Nb(1)–C(6) 2.398 (6); Nb(1)–C(7) 2.357 (6).

ning caused rapid reduction in peak currents, particularly for the return cathodic wave. Usually, after ca. five cycles response was severely diminished, indicating that the electrode had been fouled (indeed, cleaning the working electrode allowed brief continuation of the experiment). The value of $E_{1/2} = -1.18 \pm 0.01$ V for the $3^+/3$ couple is that obtained over five independent experiments. No further peaks were found at more negative potential up to the solvent discharge.

Chemical Oxidation of [Nb(η-C_7H_7)(η-C_5H_4R)]. Treament of **2** in thf with 1 equiv of ferrocenium hexafluorophosphate gave red microcrystals of [Nb(η-C_7H_7)(η-C_5H_5)(thf)][PF_6] (**4**) in 70% yield. The substituted cyclopentadienyl analogue [Nb(η-C_7H_7)(η-C_5H_4Me)(thf)][PF_6] (**4a**) was prepared similarly from **2a**. The compounds **4** and **4a** are virtually insoluble in thf, but very soluble in dichloromethane in which they are quite stable in the absence of air and water. The crystalline solids are only slightly air-sensitive.

Single crystals of **4a** were grown by slow-cooling of a dichloromethane/petroleum ether solution to −25 °C. A single-crystal X-ray diffraction study was performed.[3] (Bond lengths and angles, fractional atomic coordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.) The molecular (cation) structure is given in Figure 6 and is as proposed from NMR studies, with η-cycloheptatrienyl and η-methylcyclopentadienyl rings, and a single coordinated thf ligand. Surprisingly, the η-cycloheptatrienyl ring in this compound does not appear to be planar. The Nb–C distances between the η-cycloheptatrienyl ring and the metal center are given in the caption to Figure 6. The seven-membered ring is "dished" and an attempt to restrain it to within the usual limits of planarity led to a significant lowering of the goodness of fit of the X-ray data to the model.[3]

It was found that the CVs of **4** and **4a** in thf were indistinguishable from those of the neutral complexes **4** and **5**. From this we can infer that in both cases, the couple observed by CV is that depicted in eq 2, and not a simple $[16e]^+/[17e]$ process. It might be expected that the rate of coordination of thf (which is present in large excess) is higher than that of the heterogeneous charge-transfer step and, so, does not affect the reversibility of the couple.



(2)

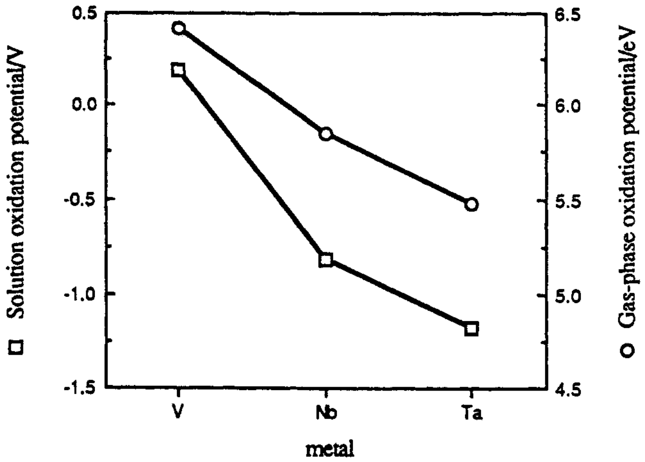


Figure 7. Gas-phase first ionization energies and solution oxidation potential of [V(η-C_7H_7)(η-C_5H_5)] (1), [Nb(η-C_7H_7)(η-C_5H_5)] (2), and [Ta(η-C_7H_7)(η-C_5H_4Me)] (3).

Figure 7 illustrates the group trends observed in both the gas-phase first IEs and solution (acetonitrile) oxidation potentials for [M(η-C_7H_7)(η-C_5H_5)]. As the group is descended, it becomse progressively easier to oxidize these compounds in the gas phase. The difference between gas-phase and solution oxidation potentials increases markedly as we go from vanadium to niobium. Between niobium and tantalum, however, the difference is virtually constant. This would be consistent with there being solvation by thf of the first-formed cations [M(η-C_7H_7)(η-C_5H_5)]$^+$ for niobium and tantalum but not for the vanadium analogue. Thus the 16 valence-electron compound [V(η-C_7H_7)(η-C_5H_5)]$^+$ does not form stable adducts with Lewis bases.[26] In support of this we note that neither [Ti(η-arene)$_2$][27] nor [V(η-arene)$_2$]$^+$[28] forms stable adducts, but the second-row metal complexes [Zr(η-toluene)$_2$(PMe_3)][29] and [Nb(η-toluene)$_2$(PMe_3)]BF_4[30] are quite stable. It seems that the smaller size of the metal in these compounds gives rise to greater restrictions on ligand bonding by limiting the bending back of the rings to accommodate the incoming ligand.

Reactions of **4** and **4a** with other potential 2-electron donors have been investigated. A red solution of [Nb(η-C_7H_7)(η-C_5H_4Me)(thf)][PF_6] in dichloromethane reacted readily with trimethylphosphine to give bright yellow cuboidal crystals of [Nb(η-C_7H_7)(η-C_5H_4Me)(PMe_3)][PF_6] (**5**) in 83% yield. Treatment of **4** in dichloromethane with carbon monoxide (1 atm) gave a green solution which yielded, on addition of petroleum ether, a green solid, **6**, which was unstable in the absence of free CO. We were unable to obtain satisfactory microanalytical data for **6**, but the ^1H NMR and infrared spectra were consistent with the formation of the CO adduct [Nb(η-C_7H_7)(η-C_5H_4Me)(CO)][PF_6]. The very high ν(C≡O) frequency (2086 cm^{-1}) for **6** corresponds to the presence of a weak M—CO bond. Treatment of **4** or **4a** with ethene, ethyne, dihydrogen, or carbon dioxide gave no reactions.

---

(26) Müller, J., Göser, P.; Laubereau, P. *J. Organomet. Chem.* **1968**, *14*, 7.

(27) Anthony, M. T.; Green, M. L. H.; Young, D. *J. Chem. Soc., Dalton Trans.* **1975**, 1419.

(28) Calderazzo, F. *Inorg. Chem.* **1964**, *3*, 810.

(29) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

(30) Brandy, J. A.; Prout, K.; Cloke, F. G. N.; de Lemos, H. C.; Wallis, J. M. *J. Chem. Soc., Dalton Trans.* **1988**, 1475.

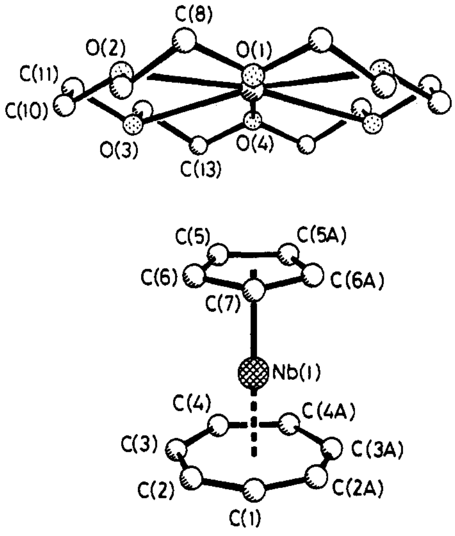


Figure 8. Molecular structures of the cationic and anionic units of [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (7). (Hydrogen atoms are omitted for clarity.) Selected bond lengths (Å): C(1)–C(2) 1.333 95); C(2)–C(3) 1.361 (6); C(3)–C(4) 1.417 (6); C(4)–C(4A) 1.471 (8); C(7)–C(6) 1.382 (5); C(6)–C(5) 1.373 (5); C(5)–C(5A) 1.393 (6).

Chemical Reduction of [Nb(η-C_7H_7)(η-C_5H_4R)]. We have shown that the 17 valence-electron complexes **2** and **2a** undergo reversible reduction at ca. −2.40 mV in thf vs the SCE. Accordingly, red-brown solutions of **4** and **5** in thf react readily with a freshly prepared potassium film to give extremely air-sensitive blue solutions, which were presumed to contain the anionic species [Nb(η-C_7H_7)(η-C_5H_4R)]$^-$ as their potassium salts, K[Nb(η-C_7H_7)(η-C_5H_4R)] (R = H, Me).

Sandwich anions such as [Nb(η-C_7H_7)(η-C_5H_4R)]$^-$ are quite rare, and few have been fully characterized. The 17 valence-electron **1** is not reduced in thf before solvent discharge,[31] although the analogous 18 valence-electron chromium system undergoes a 1-electron reduction step to give [Cr(η-C_7H_7)(η-C_5H_5)]$^-$ which was detected in solution by ESR spectroscopy.[32] The 18 valence-electron complex Na[Mn(η-C_5Me_5)$_2$] is part of a three-membered series of well-characterized manganocenes [Mn(η-C_5Me_5)$_2$]^n (n = +1, 0, −1).[33]

It was found that large blue crystals of [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (**7**) could be obtained by addition of a freshly prepared solution of K[Nb(η-C_7H_7)(η-C_5H_5)] in thf to 1 equiv of pure 18-crown-6, and storing the mixture at 0 °C. Details of the crystal structure of **7** have been described elsewhere.[3] (Bond lengths and angles, fractional atomic coordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.) Views of the molecular structures of the anionic and cationic units of **7** are shown in Figure 8. The two rings are near parallel (angle between planes ≈ 1.3°), and the angle subtended at niobium by the normals to the two ring centroids is ≈ 176.8°. The HOMO of the sandwich anion here is expected to be a largely nonbonding Nb 4d$_{z^2}$ orbital oriented toward the centroids of the two rings, and hence the parallel structure is as expected. A crystallographic mirror plane passes through C1, the midpoint of C4 and C4A, and the niobium atom. The [K(18-crown-6)]$^+$ ion displays the expected structural features.

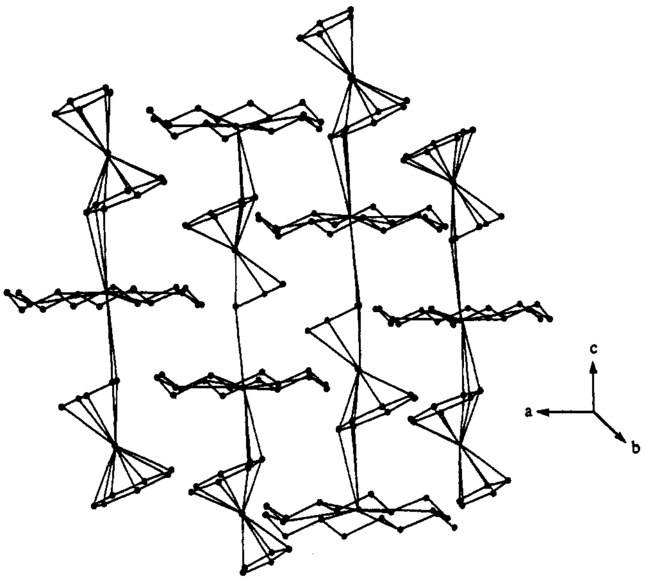


Figure 9. Crystal structure of [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (7), viewed along the crystallographic *b* axis. (Hydrogen atoms are omitted for clarity.)

Table VI. Some K–C(carbocycle) Distances

compd	K–(C_{ring})/Å	ref
[K(dme)]$_2$[Yb(η-C_8H_8)$_2$]	3.02	35
[K(thf)(dioxane)][V(η-$C_6H_3Me_3$)$_2$]	3.19	36
[K(tmeda)][fluorenyl]	3.32	43
[K(diglyme)][Ce(η-C_8H_8)$_2$]	3.16	34
[K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)]	3.00 (K–C1)	this work
	3.21 (K–C2,2A)	this work
	3.34 (K–C5,5A)	this work

Figure 9 shows views of the crystal structure of **7**, in which the cations and anions are joined alternately in an infinite distorted chain. This packing arrangement contrasts markedly with the structures of [K(diglyme)][Ce(η-C_8H_8)$_2$][34] and [K(dme)]$_2$[Yb(η-C_8H_8)$_2$],[35] which consist of quadruple and quintuple ion pairs, respectively (since the interactions within the [M(η-C_8H_8)$_2$]$^{n-}$ unit are also essentially ionic[35]). A full description of the crystal structure of [K(thf)(dioxane)][V(η-mes)$_2$][36] has not yet been appeared, although it seems that the overall structure is a zigzag arrangement, analogous to that of [Na(tmeda)][C_5H_5].[37]

The mode of cation/anion coordination in **7** is most unusual in comparison with the examples described above in that the alkali-metal ion is not equidistant from each of the carbons of a particular ring. Table VI lists some K–C distances and indicates that in comparison with the range of distances found elsewhere, three carbons of the (η-C_7H_7) ring (C1, C2, C2A) lie close to the potassium. The two carbons of the η-C_5H_5 ring closest to potassium (C_5, C5A) lie at the upper end of the spread of K–C bonding distances. Thus the potassium can be described as having a coordinated (η^3-C_7H_7) moiety and a more weakly bound (η^2-C_5H_5) ring.

The intraring C–C bond lengths in **7** are given in the caption to Figure 8, from which it can be seen that there are no significant differences for the (η-C_5H_5) ring, but that for the (η-C_7H_7) ring the C–C distances between carbons

---

[31] Gulick, W. M.; Geske, D. H. *Inorg. Chem.* **1967**, *6*, 1320.

[32] Elschenbroich, Ch.; Gerson, F.; Stohler, F. *J. Am. Chem. Soc.* **1973**, *95*, 6956.

[33] Robbins, J. L.; Edelstein, N. M.; Copper, S. R.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3853.

[34] Hodgson, K. O.; Raymund, K. N. *Inorg. Chem.* **1972**, *11*, 3030.

[35] Kinsley, S. A.; Streitwieser, A.; Zalkin, Z. *Organometallics* **1985**, *4*, 52.

[36] Fochi, G.; Braga, D.; Sabatino, P. *Organometallics* **1988**, *7*, 565.

[37] Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1979**, *175*, 21.

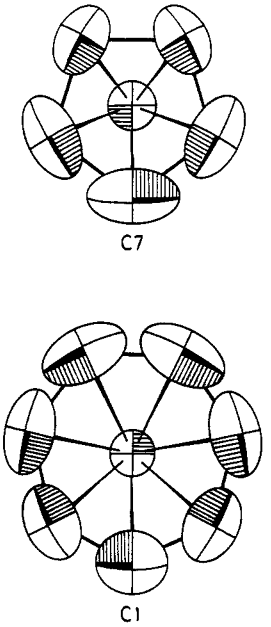


Figure 10. Thermal ellipsoids of the carbocyclic rings of the anionic unit of [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (7).

bonded to potassium (C1, C2, and C2A) are considerably shorter than the rest. In fact, the distances found here lie in a range ca. 0.07 Å longer (C4–C4A) to 0.07 Å shorter (C1–C2) than those found for other (η-C_7H_7) complexes (ca. 1.40 Å).[38] Figure 10 shows thermal ellipsoid plots for the (η-C_5H_5) and (η-C_7H_7) rings of 7. The relative sizes of the ellipsoids can be taken as an indication of the amount of thermal motion occurring for a particular atom. It can be seen that the smallest thermal ellipsoids are found for carbon atoms nearest the potasssium and that the thermal motion increases for the others. This observation suggests the presence of a librational motion with a pivot center closer to C1, C2, and C2A. In other words the ring appears to be librating under the influence of both the niobium and potassium centers. It seems that the variation in bond lengths in the C_7 ring is due to the proximity of the [K(18-crown-6)]$^+$ ion to one side of the η-cycloheptatrienyl ring, and the subsequent uneven buildup of electron density is responsible for the restricted librational motion of the rings.

Treatment of a blue solution of K[Nb(η-C_7H_7)(η-C_5H_4Me)] in thf at −80 °C with 1 equiv of iodomethane gave petroleum ether soluble red needles of [Nb(η-C_7H_7)(η-C_5H_4Me)Me] (8) in 72% yield. We note that K[Nb(η-toluene)$_2$], which is valence-isoelectronic with K[Nb(η-C_7H_7)(η-C_5H_4Me)], reacts in a similar manner with iodomethane at low temperature to give [Nb(η-toluene)$_2$Me], analogous to 8.[39]

The ^{1}H NMR spectrum of a red solution of 8 in benzene-d_6 showed bands consistent with the presence of (η-C_7H_7) and (η-C_5H_4Me) rings, as well as a singlet at 0.11 ppm assigned to a Nb–CH_3 group. The ^{13}C NMR spectrum showed no signal for the methyl carbon, presumably because of quadrupolar broadening by the niobium nucleus ($I = {}^9/_2$). Similar NMR spectroscopic behavior is displayed by [Nb(η-toluene)$_2$Me],[39] although in [Nb(η-C_5H_5)$_2$(η^2-C_2H_4)Et] the ethyl CH_2 group appears as a broad triplet at 11.2 ppm in the ^{13}C NMR.[40]

Solid 8 is air-sensitive and slightly thermally unstable. Attempted sublimation at ca. 10^{-4} Torr and 50 °C led to clean decomposition to **2a**, as evidenced by microanalysis and mass spectrometry.

Conclusions

Though the covalent nature of the majority of transition-metal complexes is recognized, most chemists still find it useful to assign a formal oxidation state to the metal in a complex. That this presents a problem for several ligand classes is well-known. The assignment of charge to a ligand in a formal oxidation state assignment requires that the ligand is "removed" from the metal with a full shell. This presents a particular problem when the neutral ligand has a doubly degenerate HOMO occupied by only 1 electron; examples of this type of ligand are NO (coordinated in a linear mode) and (η-C_7H_7). The HOMO, in such cases, has an intrinsic electronegativity similar to that of the metal if not greater, implying a real charge shift from metal to ligand. The normal way of handling these ligands is to classify them as monocations rather than anions with charges of −3. This leads, for example, to assigning an oxidation state of −IV to Cr in Cr(NO)$_4$ and treating the Cr as a d^{10} ion.

A pragmatic approach to classification of the cycloheptatrienyl compounds examined in this work is to define their electron number, namely 17, and describe them as d^1. We have presented evidence above that there is only 1 electron of predominant d character, the 4 e_2 electrons being extensively, though not exclusively delocalized onto the C_7 ring. In this context the redox chemistry of these complexes with formation of monoanion and monocation is readily understood.

If one seeks a formal classification of the C_7H_7 ligand, it would seem to us more useful to treat it in the covalent context, in which its bonding undoubtedly falls, and regard it as a 7-electron donor and a trivalent ligand. In which case it is clear that the metal is required to provide 3 electrons to form a satisfactory bond to the η-C_7H_7 ring.

Experimental Section

All manipulations and reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen which had been purified by passage through a column containing BTS catalyst and 5-Å molecular sieves. Solvents were predried over activated 5-Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene, petroleum ether [bp 100–120 °C]), or sodium–potassium alloy (petroleum ether [bp 40–60 °C], diethyl ether, and pentane) under a slow passage of nitrogen. Deuterated solvents were dried using Na/K alloy (benzene-d_6 and toluene-d_8) or phosphorus pentoxide (dichloromethane-d_2). NMR samples were made up in the drybox, and the tubes were sealed in vacuo. Cycloheptatriene (tech., Aldrich) was distilled in air then degassed. Celite 545 Filtration Aid (Koch-Light) was dried at 180 °C overnight before use. Iodomethane, iodoethane, and bromoprop-2-ene were dried over 5-Å molecular sieves and then distilled. Potassium film was prepared in an evacuated 250-cm^3 Schlenk flask by subliming a clean piece of potassium (ca. 150 mg) into the cooled lower portion of the tube using a heat gun. The following were prepared by standard methods: [Nb(η-C_5H_5)Cl_4], [Nb(η-C_5H_4Me)Cl_4] and [Ta(η-C_5H_4Me)Cl_4],[41] and [V(η-C_7H_7)(η-C_5H_5)].[4]

The PE spectra were obtained using a PES laboratories 0078 spectrometer interfaced with a Research Machines 380Z microcomputer. Both He I (21.22 eV) and He II (40.81 eV) radiation were used for spectral aquisition. Data were collected by repeated

---

[38] Scott, P. Ph.D. *Thesis*, Oxford, U.K., 1991.

[39] Green, M. L. H.; O'Hare, D.; Watkin, J. G. *J. Chem. Soc.*, Chem. *Commun.* **1989**, 698.

[40] Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

[41] Bunker, M. J.; De Cian, A.; Green, M. L. H.; Moreau, J. J. E.; Siganporia, N. *J. Chem. Soc.*, Dalton *Trans.* **1980**, 2155.

scans and the spectra calibrated with He, Xe, and N_2.

IR spectra were recorded as Nujol mulls in CsI plates on a Mattson Polaris or on a Perkin-Elmer 1510 FT-IR interferometer. NMR spectra were recorded on a Brüker AM-300 [^{1}H (300 MHz), ^{13}C (75.43 MHz), ^{31}P (121.44 MHz)] spectrometer. Two-dimensional NMR spectra were acquired using standard Brüker software and processed using an ASPECT 3000 computer. Low-resolution electron impact mass spectra were obtained on an AEI MS 302 mass spectrometer by Dr. R. Speel of this laboratory or by the SERC mass spectrometry service, University College, Swansea. Elemental analyses were performed by Analytische Laboratorien, Elbach, Germany. ESR spectra were performed by Dr. A. McCamley at the University of Sussex. CV studies were performed using an URSAR electronics potentiostat with external digital voltmeter and Lloyd PL3 fast XY recorder. The cell used was adapted from that used by Bard and Faulkner[42] modified for "Schlenk" operation. It comprised a vacuum-tight chamber fitted with inlets for a platinum-disk working electrode, a platinum-gauze auxiliary electrode, and a silver-wire pseudoreference electrode. Typically, 10–12 cm^3 of electrolyte solution (containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate) and ca. 2 mg of solid sample were used.

(η-Cycloheptatrienyl)(η-cyclopentadienyl)niobium (2). A partially dissolved suspension of [Nb(η-C_5H_5)Cl_4[(8.0 g, 27 mmol) in thf (300 cm^3) and cycloheptatriene (50 cm^3) was cooled to −80 °C and transferred using a wide-bore cannula onto magnesium turnings (5 g, excess) and the mixture was stirred vigorously for 20 h. The resulting dark green solution was decanted from the excess magnesium, and the volatiles were removed under reduced pressure to give a red-brown solid. Diethyl ether extracts (2 × 100 cm^3) were evaporated to dryness, and the residue was sublimed at 140 °C and 5×10^{-2} mbar in portions onto a liquid nitrogen cooled probe to give a purple-red solid. Yield: 2.7 g, 40%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)niobium (2a). A solution of [Nb(η-C_5H_4Me)Cl_4] (7.8 g, 25 mmol) in thf (500 cm^3) and cycloheptatriene (40 cm^3) was cooled to −80 °C and transferred onto magnesium (8 g). The mixture was stirred vigorously and allowed to warm to room temperature. After 12 h the dark solution was decanted and the volatiles were removed under reduced pressure. The resulting brown residue was extracted with petroleum ether (40–60 °C, 4 × 200 cm^3). The combined filtered extracts were reduced in volume to 100 cm^3 and filtered again before cooling to −80 °C. Dark maroon crystals deposited, which were isolated by filtration and washed with cold petroleum ether (40–60 °C, 2 × 20 cm^3) before drying in vacuo. A further crop of crystals was obtained from the mother liquor by a similar procedure. Combined yield: 2.8 g, 43%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)tantalum (3). A solution of [Ta(η-C_5H_4Me)Cl_4] (5.0 g, 14.2 mmol) in thf (200 cm^3) and cycloheptatriene (25 cm^3) was cooled to −80 °C and transferred onto magnesium (5 g). After stirring vigorously for 30 min the solution was green and gradually turned dark red over 3 h. The solution was decanted and the volatiles removed under reduced pressure to give a dark solid. This was extracted with petroleum ether (40–60 °C, 4 × 100 cm^3) and the combined filtered extracts were reduced in volume to 80 cm^3. The solution was filtered and cooled to −80 °C to yield oily dark crystals overnight (ca. 1 g). These were washed with petroleum ether (40–60 °C, 20 cm^3) and sublimed at 80 °C and 5×10^{-2} mbar in portions onto a liquid nitrogen cooled probe. The purple sublimates were combined and crystallized from petroleum ether (40–60 °C) to give large blue cubes. Yield: 0.6 g, 12%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)(tetrahydrofuran)niobium Hexafluorophosphate (4a). A solution of [Nb(η-C_7H_7)(η-C_5H_4Me)] (2a) (1.0 g, 3.8 mmol) in thf (60 cm^3) was transferred onto solid ferrocenium hexafluorophosphate (1.28 g, 3.9 mmol). Dissolution of the ferrocenium salt accompanied a color change from red-brown to bright red. A red crystalline precipitate was deposited which was isolated by filtration and dissolved in dichloromethane (20 cm^3). Petroleum ether (40–60 °C) was added dropwise until a persistent red precipitate formed. The solution was filtered and cooled to −25 °C overnight to give red cubes which were isolated by filtration and dried in vacuo. Yield: 1.38 g, 76%.

The unsubstituted cyclopentadienyl analogue [Nb(η-C_7H_7)(η-C_5H_5)(thf)] PF_6 (4) was prepared similarly from [Nb(η-C_7H_7)(η-C_5H_5)] (2) and 1 equiv of ferrocenium hexafluorophosphate. Yield: 70%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)(trimethylphosphine)niobium Hexafluorophosphate (5). A solution of [Nb(η-C_7H_7)(η-C_5H_4Me)(thf)]PF_6 (4a) (250 mg, 0.52 mmol) in dichloromethane (20 cm^3) was cooled to −196 °C in vacuo and trimethylphosphine (0.15 cm^3, 1.4 mmol) was condensed into the vessel. The mixture was allowed to warm to room temperature under nitrogen with stirring. The color changed rapidly from red to yellow as the solvent melted. The volatiles were removed under reduced pressure, and the yellow residue was dissolved in dichloromethane (10 cm^3). Petroleum ether was added dropwise until the yellow precipitate was persistent. The solution was filtered and cooled to −25 °C. Yellow cubes formed overnight which were isolated by filtration and dried in vacuo. Yield: 0.21 g, 83%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)carbonylniobium Hexafluorophosphate (6). A solution of [Nb(η-C_7H_7)(η-C_5H_5)(thf)]PF_6 (4) (250 mg, 0.54 mmol) in dichloromethane (20 cm^3) was exposed to 1 atm of carbon monoxide with stirring. The color changed rapidly from red to green. Petroleum ether (40–60 °C, 30 cm^3) was added to give a green precipitate (ca. 150 mg) which was isolated by filtration and dried in a stream of carbon monoxide for 0.5 h. The solid turned purple-brown on exposure to nitrogen or in vacuo.

Potassium (18-Crown-6)(η-cycloheptatrienyl)(cyclopentadienyl)niobium (7). Owing to the extreme air and water sensitivity of [K(18-crown-6)][Nb(η-C_7H_7)(η-C_5H_5)] (7), this experiment was performed in an apparatus consisting of two 150-cm^3 Schlenk tubes connected by a frit. This is referred to here as an "H-tube".

A solution of [Nb(η-C_7H_7)(η-C_5H_5)] (2) (0.25 g, 1.0 mmol) in thf (30 cm^3) was transferred onto freshly prepared potassium film in one arm of the H-tube. After 10 min the blue solution thus formed was filtered through the glass frit onto solid 18-crown-6 (260 mg, 1.0 mmol) and the mixture was shaken briefly to dissolve the solid. Cooling the solution slowly to 0 °C caused deposition of large blue cubes. Yield: 0.46 g, 83%.

(η-Cycloheptatrienyl)(η-methylcyclopentadienyl)methylniobium (8). A solution of [Nb(η-C_7H_7)(η-C_5H_4Me)] (2a) (250 mg, 0.95 mmol) in thf (30 cm^3) was transferred onto a freshly prepared potassium film. The red-brown solution rapidly turned purple-blue. After 10 min the solution was transferred to a clean vessel and cooled to −80 °C. Iodomethane (0.06 cm^3, 0.96 mmol) was added, and the mixture was stirred. The blue solution rapidly turned red. The mixture was allowed to warm to room temperature, and the volatiles were removed under reduced pressure to give a brown solid. This was extracted with petroleum ether (40–60 °C, 2 × 50 cm^3). The combined filtered extracts were reduced in volume to 15 cm^3, filtered, and cooled to −80 °C. Red crystals formed overnight which were isolated by filtration and washed with a small amount of cold petroleum ether (40–60 °C) before drying in vacuo. Yield: 0.19 g, 72%.

Acknowledgment. We thank the SERC for Quota awards to P.S. and N.K., St. Catherine's College, Oxford for a Light Senior Scholarship (to N.K.) and Wolfson College, Oxford, for a Junior Research Fellowship (to P.M.).

OM9200971

---

(42) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 6.

(43) Zerger, R.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 5441.