suggesting that they are also trans isomers. However, the rather broad, lowest energy band in **13** and **14** was not resolved into two bands as in the case of Fischer's compounds. As is normally observed in analogous tunsten and chromium carbonyl complexes, the ν(CO) values of the tungsten complex **14** are higher than the corresponding values of the chromium complex **13**. There is also observed a band of medium intensity at ca. 1600 cm^{-1} which Fischer has attributed earlier[28] to a CN stretching frequency. The relative position of this ν(CN) mode emphasizes that the CNMe$_2$ unit in these complexes is best described as having both carbene and carbyne character; i.e., the following resonance forms are both of importance in describing their ground electronic states.

$$\{(\mathrm{Ph_3Sn})(\mathrm{CO})_4\mathrm{M}{\equiv}\mathrm{C}{-}\mathrm{NMe_2} \leftrightarrow (\mathrm{Ph_3Sn})(\mathrm{CO})_4\bar{\mathrm{M}}{=}\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{Me_2}\}$$

Proton NMR spectra of **13** and **14** are also entirely consistent with the proposed formulations. On the basis of these results, we suggest that other highly nucleophilic organotin derivatives of carbonyl anions may also be useful precursors to analogous carbyne complexes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE 82-10496) for continuing support of this research.

Registry No. **1**, 67202-48-6; **2**, 67202-50-0; **3**, 67202-52-2; **4**, 67202-54-4; **5**, 86129-00-2; **6**, 86129-01-3; **7**, 86129-03-5; **8**, 86129-05-7; **9**, 86129-07-9; **10**, 86129-09-1; **11**, 86129-11-5; **12**, 86129-13-7; **13**, 86129-14-8; **14**, 86129-15-9; Na$_4$[Cr(CO)$_4$], 67202-62-4; Ph$_3$SnCl, 639-58-7; Et$_4$NBr, 71-91-0; Ph$_3$SnLi, 4167-90-2; (TMED)Cr(CO)$_4$, 21136-10-7; (NBD)Mo(CO)$_4$, 12146-37-1; Na$_4$[W(CO)$_4$], 67202-46-4; (COD)W(CO)$_4$, 12129-70-3; Li$_2$[(Ph$_3$Sn)$_2$Cr(CO)$_4$], 86129-16-0; Li$_2$[(Ph$_3$Sn)$_2$W(CO)$_4$], 86129-17-1; (TMED)W(CO)$_4$, 15024-58-5; CH$_3$I, 74-88-4; CH$_3$CN, 75-05-8; [Et$_4$N][(Ph$_3$Sn)Cr(CO)$_5$], 55997-66-5; Ph$_3$P, 603-35-0; [Me$_2$NCCl$_2$]Cl, 33842-02-3; Sn, 7440-31-5; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7.

Electron Spin Resonance and Photoelectron Studies of Neutral Bis(η-arene)metal Compounds (Metal = Ti, V, Nb, Ta, Mo, and W)†

F. Geoffrey N. Cloke, Alan N. Dix, Jennifer C. Green,* Robin N. Perutz,* and Elaine A. Seddon

Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, United Kingdom

Received January 12, 1983

The electronic structure of several bis(η-arene)metal complexes, synthesized by the metal vapor method, has been examined by electron spin resonance (ESR) and photoelectron spectroscopy (PES). The ESR spectra of Nb(η-arene)$_2$ and Ta(η-C$_6$H$_6$)$_2$ in frozen toluene at 77 K are axial and show $g_\parallel \approx 2$ and $g_\perp = 1.94$–1.98 consistent with a ^{2}A$_1$ ground state. The spectra show structure arising from coupling to the protons and highly anisotropic coupling to the metal nuclei. The extent of delocalization onto the ring protons is little affected by the arene in the series Nb(η-arene)$_2$ (arene = benzene, toluene, mesitylene), but a substantial increase is observed in the proton coupling down the series V(η-C$_6$H$_6$)$_2$, Nb(η-C$_6$H$_6$)$_2$, and Ta(η-C$_6$H$_6$)$_2$ (A^H = 4.1, 5.1, and 6.1 G, respectively). Additionally, solution ESR spectra at 300 K show considerable increases in the metal (n + 1)s electron density down the group. The PE spectra were assigned with the aid of comparisons between He I and He II spectra. The spectra of the d^6 complexes W(η-arene)$_2$ (arene = benzene, toluene, mesitylene) are consistent with a ^{2}A$_1$ ground state for the cation (IE = 5.2–5.4 eV) with a ^{2}E$_{5/2}$/^{2}E$_{3/2}$ doublet appearing ~1.2 eV to higher energy. The first ionizations of the d^5 complexes Nb(η-arene)$_2$ are assigned to ^{1}A$_1$ ion states with ^{3}E$_2$ and ^{1}E$_2$ states appearing at higher IE. The ion ground state of Cr(η-C$_5$H$_5$)(η-C$_6$H$_6$) is shown to be the ^{3}E$_2$ state, while the lowest ionization of its molybdenum analogue consists of overlapping bands from the ^{3}E$_2$ and ^{1}A$_1$ ion states. The PE spectra of Ti(η-C$_6$H$_6$)$_2$ and Ti(η-C$_6$H$_5$Me)$_2$ are consistent with a ^{1}A$_1$ ground state leading to a ^{2}E$_2$ ion ground state. Evidence is presented for a back-bonding interaction of e$_{2g}$ symmetry between the metal and the arene ring.

Introduction

A variety of new bis(η-arene)metal complexes of titanium and of the second- and third-row metals of groups 5 and 6 have recently become available through metal-vapor synthesis.[1-3] In this paper we examine the electronic structure of these complexes by using electron spin resonance (ESR) and photoelectron spectroscopy (PES). The electron spin resonance spectra of several d^5 bis(arene) compounds of V and Cr have been reported in solution, in glasses, and doped into related diamagnetic hosts.[4-7] The spectra are typically axial with $g \approx 2.00$ and $g \approx 1.98$, and show very anisotropic metal hyperfine coupling (e.g., V(η-C$_6$H$_6$)$_2$, $A_\perp{}^\mathrm{V} = 92.1$, $A_\parallel{}^\mathrm{V} = 6$ G; Cr(η-C$_6$H$_6$)$_2{}^+$, $A_\perp{}^\mathrm{Cr} = 26.9$, $A_\parallel{}^\mathrm{Cr} = 0.5$ G).[5,7] The proton hyperfine splitting is often highly resolved and is closer to isotropic (e.g., V(η-C$_6$H$_6$)$_2$, $A_\parallel{}^\mathrm{H} = 3.75$, $A^\mathrm{H}{}_\mathrm{av} = 4.12$; Cr($\eta$-C$_6H_6$)$_2{}^+$, $A_\parallel{}^\mathrm{H} = 3.1$,

---

† No reprints available.

(1) Benfield, F. W. S.; Green, M. L. H.; Ogden, J. S.; Young, D. *J. Chem. Soc., Chem. Commun.* **1973**, 866. Anthony, M.; Green, M. L. H.; Young, D. *J. Chem. Soc., Dalton Trans.* **1975**, 1419.

(2) Cloke, F. G. N.; Morris, G. E.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 72.

(3) Cloke, F. G. N.; Green, M. L. H.; Price, D. H. *J. Chem. Soc., Chem. Commun.* **1978**, 431. Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

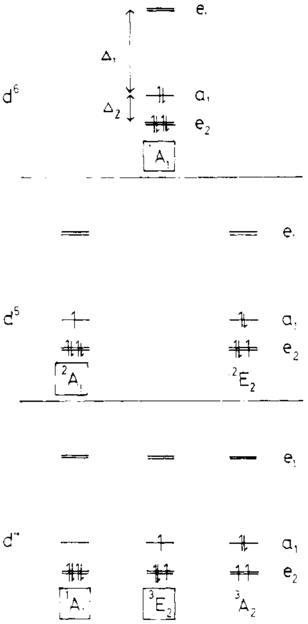
(4) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45 and references therein. Green, J. C. *Ibid.* **1981**, *43*, 37.

(5) Schweiger, A.; Wolf, R.; Gunthard, H. H.; Ammeter, J. H.; Deiss, E. *Chem. Phys. Lett.* **1980**, *71*, 117.

(6) Elschenbroich, C.; Heck, J. *Angew Chem., Int. Ed. Engl.* **1981**, *21*, 267.

(7) Prins, R.; Reinders, F. J. *Chem. Phys. Lett.* **1969**, *3*, 45.

Scheme I. Possible Ground-State Configurations of M(η-arene)$_2$ [a]



[a] Those most commonly adopted are marked by a box (g and u symbols are omitted here and elsewhere for simplicity).

A^{H}_{av} = 3.46 G).[5,7] The g values are in accord with the expectations of first-order perturbation theory[8] for a $^2A_1$ ground state with the unpaired electron in a d_{z^2} orbital (Scheme I)

$$g_{\parallel} = g_e$$
$$g_{\perp} = g_e - 6\lambda/\Delta_1 \qquad (1)$$

(where Δ_1 is the separation between the a_1 and unoccupied e_1 levels).[4] The values of $g_{\perp}$ decrease slightly down the group (M = Cr, Mo, W),[9] although not nearly as much as expected from changes in λ alone. The signs of the chromium hyperfine coupling (Cr(η-C$_6$H$_6$)$_2^+$) are consistent with occupation of the d_{z^2} orbital, and A_{iso} is deduced to originate in spin polarization with no significant $3d_{z^2}$/4s mixing.[7] Wide-line nuclear magnetic resonance has been used to deduce that the proton hyperfine coupling constants of Cr(η-C$_6$H$_6$)$_2^+$ and V(η-C$_6$H$_6$)$_2$ have positive signs, while the coupling constants of the methyl protons in substituted M(η-arene)$_2$ complexes are negative.[7,10] The large positive value of A_H (ring) has been explained by dominant σ delocalization arising by mixing of the σ and π(a$_{1g}$) ring orbitals assisted by some spin polarization. The spin polarization term is negative on the ring carbon atoms, positive on ring hydrogens, and negative on substituent hydrogens. The σ delocalization is diminished and the polarization term dominates for the methyl protons.[10] It is notable that the magnitude of A^{H}_{av} (ring) is unaltered along the series V(η-C$_6$H$_6$)$_2$, V(η-C$_6$H$_5$Me)$_2$, and V(η-C$_6$H$_3$Me$_3$)$_2$ (C$_6$H$_3$Me$_3$ = mesitylene).[11] The remarkable resolution of the proton coupling in the ESR spectra has been attributed to rapid rotation of the arene rings, particularly in the benzene complexes.[5,7] Recently, the temperature dependence of the ENDOR spectrum of V(η-C$_6$H$_6$)$_2$ has been used to confirm that $A^{H}_{av} > 0$, to obtain more details of the proton hyperfine tensor, and to follow the effect of ring rotation.[5]

The PE spectra of Cr(η-C$_6$H$_6$)$_2$,[12,13] Cr(η-C$_6$H$_5$Me)$_2$, Cr(η-C$_6$H$_3$Me$_3$)$_2$, Mo(η-C$_6$H$_6$)$_2$, Mo(η-C$_6$H$_5$Me)$_2$, Mo(η-C$_6$H$_3$Me$_3$)$_2$, and V(η-C$_6$H$_3$Me$_3$)$_2$[14] have been described. The ion ground states are shown to be ^{2}A$_1$ for the group 6 compounds and ^{3}E$_2$ for the vanadium compound (Scheme I). The small full-width at half-maximum (fwhm) of the bands arising from ionizing electrons occupying an a$_{1g}$ orbital suggested that this orbital was mainly nonbonding in character. By contrast the fwhm associated with e$_{2g}$ bands indicated bonding character and back donation from the metal to the arene rings. The e$_{1g}$ and e$_{1u}$ bands may be distinguished clearly in the PE spectra of the Mo compounds, but the separation is smaller in the arene compounds of the first-row metals, indicating less covalency in these compounds.

We have examined the ESR spectra of Nb(η-arene)$_2$ (arene = C$_6$H$_6$, C$_6$D$_6$, C$_6$H$_5$Me, C$_6$H$_3$Me$_3$) and of Ta(η-C$_6$H$_6$)$_2$ in toluene solution at room temperature and in frozen solution at 77 K. For comparative purposes we also remeasured the ESR spectra of V(η-C$_6$H$_6$)$_2$ and V(η-C$_6$H$_5$Me)$_2$. Ionization energies have already been reported for the low-energy bands of Ti(η-C$_6$H$_6$)$_2$, Ti(η-C$_6$H$_5$Me)$_2$,[1] W(η-C$_6$H$_6$)$_2$, W(η-C$_6$H$_5$Me)$_2$, W(η-C$_6$H$_3$Me$_3$)$_2$,[2] Nb(η-C$_6$H$_6$)$_2$, Nb(η-C$_6$H$_5$Me)$_2$, and Nb(η-C$_6$H$_3$Me$_3$)$_2$.[3] We report here these spectra in detail and also the PE spectra of V(η-C$_6$H$_6$)$_2$, V(η-C$_6$H$_5$Me)$_2$, and Mo(η-C$_5$H$_5$)(η-C$_6$H$_6$) and the He II spectrum of Cr(η-C$_5$H$_5$)(η-C$_6$H$_6$) (the He I spectrum has been reported previously).[12] Comparison with first-row complexes allow us to establish trends in the energy levels and spin distributions in these complexes.

Experimental Section and Analysis

ESR. All of the bis(arene)metal compounds were prepared by metal-vapor synthesis using electron-beam evaporation as described in an earlier publication.[3] The products were recrystallized from light petroleum, dried, and transferred under argon in an inert-atmosphere box into the bulb of an integral ESR tube/filter device equipped with Teflon stopcocks. Toluene (BDH Aristar, purity >99.95%, distilled over sodium) was condensed onto the sample, which after dissolution, passed through a glass frit into the ESR tube. ESR spectra were recorded at X band on a Varian E109 spectrometer calibrated with MnO in MgO (g = 2.0015, A^{Mn} = 86.8 G).

The ESR spectra were simulated by using a modified version of a computer program supplied by Dr. J. B. Raynor, based on a program by Pilbrow. Spectra were calculated to second order as the weighted sum of the spectra of individual molecules oriented at a series of angles between the molecular axis and the applied field. The angles were varied from 0 to 90° in 0.1° steps. The input parameters were ν_0, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}^{M}$, $A_{\perp}^{M}$, A_{av}, and W where W is the fwhm of a Lorentzian line shape. The proton coupling was assumed to be isotropic and was introduced into the program as a first-order correction. The parameters were refined manually and a satisfactory fit (agreement to <1.5 G) was obtained in all cases without recourse to further parameters. However, no attempt was made to simulate the increase in line width away from the position where the g values are in coincidence. Thus, some fine structure in the calculated spectra remained unobserved.

The metal hyperfine coupling was corrected for orbital contributions and used to deduce anisotropic and isotropic coupling

---

(8) Goodman, B. A.; Raynor, J. B. *Avd. Inorg. Chem. Radiochem.* **1970**, *13*, 136.

(9) Hausser, K. H. *Naturwissenschaften* **1961**, *48*, 426.

(10) Anderson, S. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 4244.

(11) Heinrici-Olive, G.; Olive, S. *Z. Phys. Chem.* (*Wiesbaden*) **1967**, *56*, 223.

(12) Evans, S.; Green, J. C.; Jackson, S. E. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 249.

(13) Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

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

Table I. Measured ESR Parameters Correct to Second Order[a]

	g_{iso}	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}{}^{M}$	$A_{\perp}{}^{M}$	A^{H}
V(η-C_6H_6)$_2$	1.987 (1)	−62.7 (3)	1.998 (1)	1.9797 (5)	1.986	−2.9[b]	−92.7 (3)	4.1 (1)
V(η-C_6H_5Me)$_2$	1.984 (1)	−62.0 (3)	1.997 (1)	1.9745 (5)	1.982	−0.2[b]	−92.9 (3)	4.0 (3)
Nb(η-C_6H_6)$_2$	1.982 (1)	18 (1)	2.0010 (5)	1.9730 (5)	1.9820	93.1 (3)	−20.6 (4)	5.1 (1)
Nb(η-C_6D_6)$_2$	1.985 (1)	16.8 (3)	2.0010 (5)	1.9730 (5)	1.9820	93.6 (3)	−20.6 (4)	
Nb(η-C_6H_5Me)$_2$	1.982 (1)	23.2 (3)	1.9980 (5)	1.9705 (5)	1.9797	97.8 (3)	−13.4 (4)	5.2 (1)
Nb(η-$C_6H_3Me_3$)$_2$	1.9867 (5)	39.2 (3)	1.9985 (5)	1.9715 (5)	1.9805	112.5 (3)	−0.5 (2)	5.4 (1)
Ta(η-C_6H_6)$_2$	1.955 (2)	138 (2)	1.997 (1)	1.942 (1)	1.960	220 (2)	95.4 (5)	6.1 (2)

[a] The signs of the A values given in G are those required to give a positive value of *2B* (see Table II). [b] Calculated by using solution value of A_{iso}.

Table II. Derived ESR Parameters[a]

	2B, G	A_{iso}(corr), *G*	% *n*d	% (*n* + 1) s	% H (per proton)
V(η-C_6H_6)$_2$	58.2	−61.0	54.4	1.1	0.78
V(η-C_6H_5Me)$_2$	59.7	−59.9	55.7	1.2	0.77
Nb(η-C_6H_6)$_2$	73.8	20.2	61.6	6.7	0.99
Nb(η-C_6D_6)$_2$	74.2	20.4	61.9	6.7	
Nb(η-C_6H_5Me)$_2$	72.0	26.7	60.0	7.1	1.01
Nb(η-$C_6H_3Me_3$)$_2$	73.4	40.1	61.2	7.9	1.05
Ta(η-C_6H_6)$_2$	80.8	143.4	74.5	15.2	1.19

[a] Assuming values of $2B°$ and $A°_{iso}$ as follows: V 106.1, 933; Nb 118.6, 1530; Ta 106.2, 1399 G.

constants using the first-order equations appropriate for a $d^4_{x^2-y^2,xy}$, $d^1_{z^2}$ configuration:[8]

$$A_{\parallel} = A_{iso}{}^{corr} + 2B \qquad (2)$$

$$A_{\perp} = A_{iso}{}^{corr} - B[1 - 3.5(g_{\perp} - g_e)]$$

The values of $A_{iso}{}^{corr}$ and $2B$ were converted into approximate spin densities by using values of $2B°$ and $A°_{iso}$ calculated from the Hartree–Fock wave functions recently given by Froese–Fischer[15] using the equations

$$2B° = \mu_0\beta_N\mu_N\langle r^{-3}\rangle/5\pi a_0{}^3I$$

$$A° = 2\mu_0\beta_N\mu_N|\psi_s(0)|^2/3a_0{}^3I \qquad (3)$$

The values obtained (see Table II) for $A°_{iso}$ were not significantly different from published values,[8] but the values of $2B°$ were considerably higher. In calculating s-electron densities on the metals a contribution of $-0.4\% A°_{iso}$(inner s) (i.e., V, −72; Nb, −88; Ta, −81 G) by spin polarization was assumed.

PES. Ti(η-arene)$_2$, Nb(η-arene)$_2$, and W(η-arene)$_2$ were prepared by metal vapor synthesis as described previously.[1-3] Cr(η-C_5H_5)(η-C_6H_6) and Mo(η-C_5H_5)(η-C_6H_6) were prepared according to literature methods.[16,17] Thermal decomposition prevented us from obtaining a spectrum of Ta(η-C_6H_6)$_2$. All samples were sublimed prior to spectral measurement. The compounds were introduced into the spectrometer by sealing under vacuum in small glass tubes of appropriate diameter for the heated insert and then breaking these tubes in a bag filled with N_2 tied to the top of the airlock entrance to the main chamber. They were quickly inserted into the probe which was then introduced into the spectrometer. Spectra were measured by using a Perkin-Elmer PS16/18 photoelectron spectrometer fitted with an Helectros lamp capable of giving both He I and He II radiation. Experimental conditions are given in Table III. They were calibrated with respect to inert gases and the He($1s^{-1}$) band. Calibration was especially difficult in the case of the Ti compounds as introduction of calibrant gas resulted in disappearance of the spectrum of the compound and appearance of the spectrum of the free arene ligand. In the case of Nb(η-C_6H_6)$_2$, though the presence of low-energy bands showed that the compound was being photoionized, the intensity of the bands in the higher ionization energy (IE) region indicated the presence of free ligand; thus IE data above 8.5 eV are not available on this compound. He II spectra were obtained where practicable (see Table III).

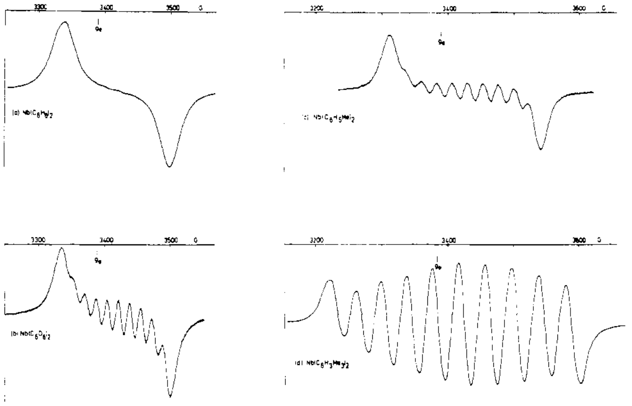


Figure 1. ESR spectra (X band) of bis(η-arene)niobium complexes in toluene solution at room-temperature: (a) Nb(η-C_6H_6)$_2$, (b) Nb(η-C_6D_6)$_2$, (c) Nb(η-C_6H_5Me)$_2$, (d) Nb(η-$C_6H_3Me_3$)$_2$. (Operating frequencies: (a) 9.498, (b) 9.504, (c) 9.503, (d) 9.485 GHz.)

Results

ESR. V(η-arene)$_2$. The spectra of V(η-C_6H_6)$_2$ and V(η-C_6H_5Me)$_2$ were very similar to the published spectra with the expected octet in the solution spectra (^{51}V, $I = {}^{5}/_{2}$, 100%).[11,18] The frozen solution spectrum of V(η-C_6H_6)$_2$ resembled the spectrum in a ferrocene host illustrated in Figure 1b of ref 5. Our analysis yields *g* and *A* values (Table I) which are close to those of ref 5 and are consistent with occupation of the d_{z^2} orbital by the unpaired electron. In that case the condition of positive $2B$ imposes negative signs on A^{V}_{iso}, $A_{\perp}{}^{V}$, and $A_{\parallel}{}^{V}$. Since the isotropic coupling to vanadium is negative, it must originate in spin polarization with almost no 4s contribution to the spin density (Table II). The analysis of the spectrum of V(η-C_6H_5Me)$_2$ yields very similar results, but the proton hyperfine coupling is less well resolved.

Nb(η-arene)$_2$. The isotropic ESR spectra of Nb(η-arene)$_2$ increased in line width in the order (η-$C_6H_3Me_3$) < (η-C_6H_5Me) < (η-C_6H_6) such that hyperfine coupling (^{93}Nb,

---

[15] Froese-Fischer, C. "The Hartree-Fock Method for Atoms", Wiley: New York, 1977.

[16] Fischer, E. O.; Breitschaft, S. *Chem. Ber.* **1966**, *99*, 2213.

[17] Green, M. L. H.; Knight, J.; Segal, J. A. *J. Chem. Soc., Chem. Commun.* **1975**, 283.

[18] Unlike the published spectra[11] of V(η-arene)$_2$ in solution, we did not resolve the proton hyperfine structure at room temperature.

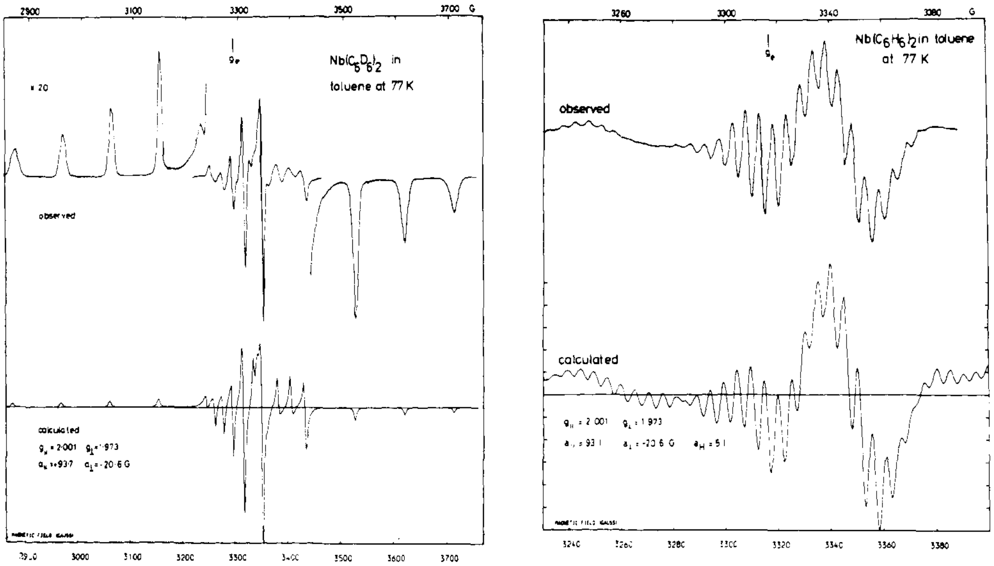


Figure 2. Left above: ESR spectrum (9.228 GHz) of Nb(η-C_6D_6)$_2$ in frozen toluene at 77 K. Note 20× expansion of outer lines. Left below: calculated spectrum with $g_\parallel$ = 2.001, $g_\perp$ = 1.973, $A_\parallel$ = 93.7 G, and $A_\perp$ = −20.6 G. Right above: central region of the Nb(η-C_6H_6)$_2$ ESR spectrum (9.229 GHz) in frozen toluene at 77 K showing overlapping ^{93}Nb and ^{1}H hyperfine coupling. Below right: calculated spectrum with $g_\parallel$ = 2.001, $g_\perp$ = 1.973, $A_\parallel$ = 93.1 G, $A_\perp$ = −20.6 G, and A^H = 5.1 G.

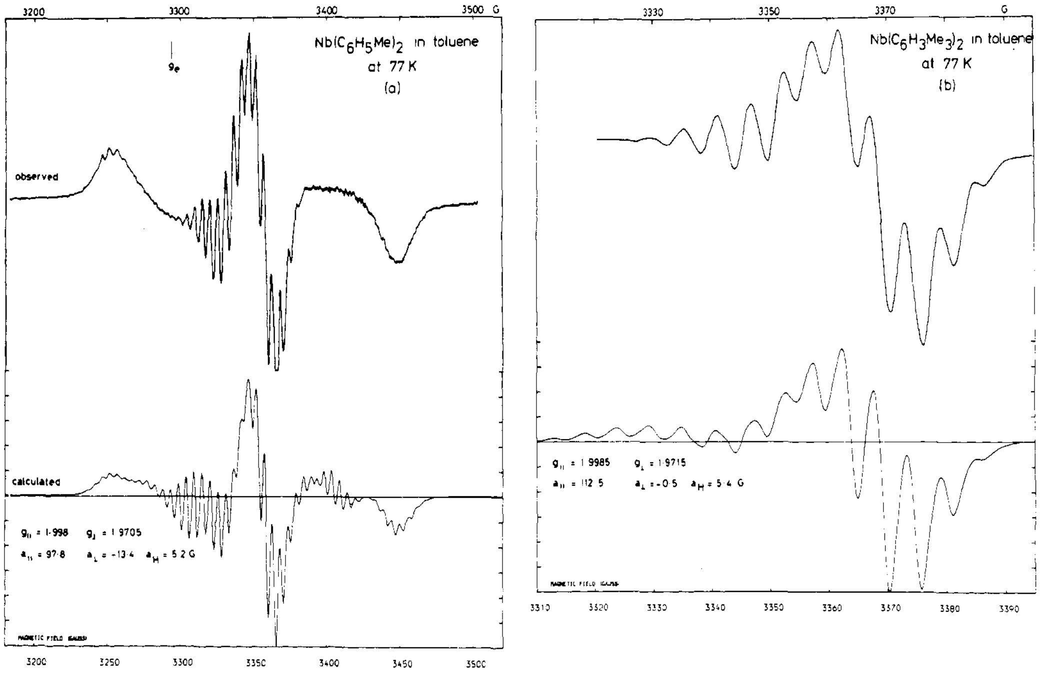


Figure 3. (a) Above: central region of the ESR spectrum (9.231 GHz) of Nb(η-C_6H_5Me)$_2$ in frozen toluene solution at 77 K showing the fifth to seventh parallel features. The sixth parallel feature lies close to the perpendicular features. Below: calculated spectrum with $g_\parallel$ = 1.998, $g_\perp$ = 1.9705, $A_\parallel$ = 97.8 G, $A_\perp$ = −13.4 G, and A^H = 5.2 G. (b) Above: central region of the ESR spectrum (9.249 GHz) of Nb(η-$C_6H_3Me_3$)$_2$ in frozen toluene solution at 77 K containing the sixth parallel feature and the perpendicular features. Below: calculated spectrum with $g_\parallel$ = 1.9985, $g_\perp$ = 1.9715, $A_\parallel$ = 112.5 G, $A_\perp$ = −0.5 G, and A = 5.4 G.

$I = {}^9/_2$, 100%) could be resolved only for Nb(η-C_6H_5Me)$_2$ and Nb(η-$C_6H_3Me_3$)$_2$ (Figure 1). Use of Nb(η-C_6D_6)$_2$ revealed the niobium coupling (Figure 1) for this complex and showed that the broadening was caused by unresolved proton coupling superimposed on decreased coupling to ^{93}Nb (Table I). The low-temperature spectrum of Nb(η-C_6H_6)$_2$ showed a regularly spaced set of parallel features with a complex group of lines in the central region of the spectrum in which the perpendicular coupling was masked by the proton hyperfine (Figure 2a). Use of Nb(η-C_6D_6)$_2$ simplified the spectrum and showed an irregularly spaced set of perpendicular features (Figure 2b). The irregularities originate in second-order effects which become important when $A_\perp^{Nb} \ll A_\parallel^{Nb}$ and are accounted for satisfactorily in the computer simulation (Figure 2b). The values derived for $g_\perp$ and $A_\perp^{Nb}$ for Nb(η-C_6D_6)$_2$ could be used without change to simulate the central region of the Nb(η-C_6H_6)$_2$ spectrum (Figure 2a). The large number of hyperfine features in this spectrum is explained by the coincidence of $A_\perp^{Nb}$ with $4A^H$. The low-temperature spectra of Nb(η-C_6H_5Me)$_2$ and Nb(η-$C_6H_3Me_3$)$_2$ show a similar pattern to Nb(η-C_6H_6)$_2$ but with increasing $A_\parallel^{Nb}$, decreasing $|A_\perp^{Nb}|$, and slight increases in A^H (Table I, Figure 3). For Nb(η-$C_6H_3Me_3$)$_2$ $|A_\perp^{Nb}| \ll A^H$ and $|A_\perp^{Nb}|$ is close to but significantly different from zero. These spectra again show second-order complications in the

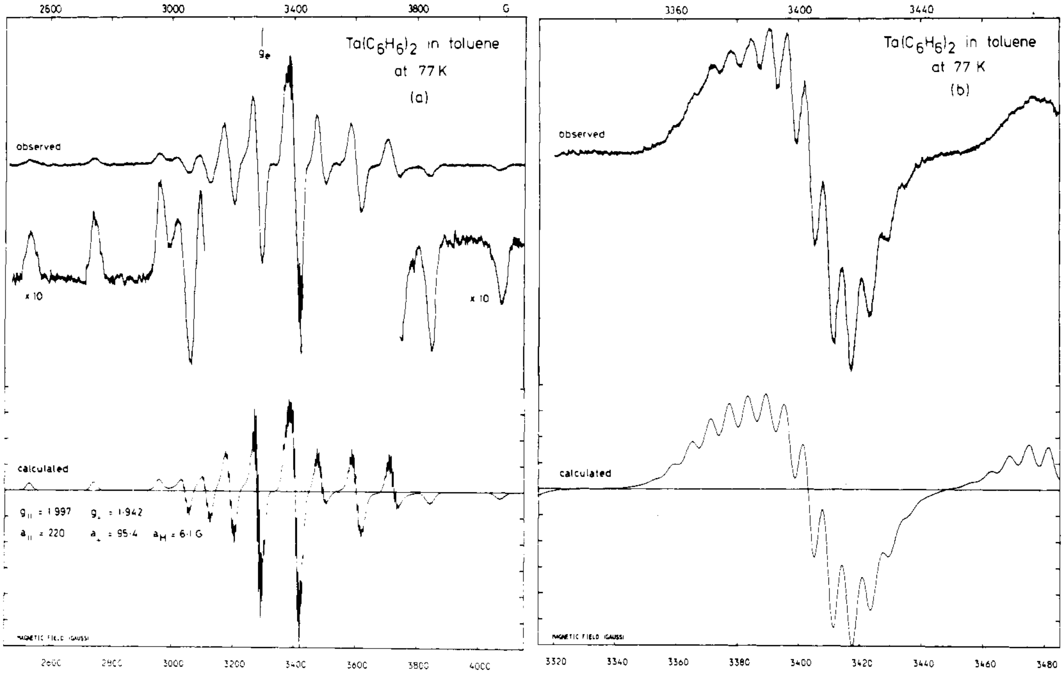


Figure 4. (a) Above: ESR spectrum (9.241 GHz) of Ta(η-C_6H_6)$_2$ in frozen toluene at 77 K. Note 10× expansion of outer parallel features. Below: calculated spectrum with $g_\parallel$ = 1.997, $g_\perp$ = 1.942, $A_\parallel$ = 220 G, $A_\perp$ = 95.4 G, and A^H = 6.1 G. (b) Above: expansion of the central line of the Ta(η-C_6H_6)$_2$ ESR spectrum showing proton hyperfine coupling on the central line where the fifth parallel and fifth perpendicular lines overlap. Below: calculated spectrum with parameters as in a.

perpendicular region which also contains the sixth parallel feature.

The g values of the niobium complexes, like their vanadium analogues, conform to the expectations for a $^2A_1$ ground state. Accordingly a positive value of $2B$ implies positive values of $A_{iso}{}^{Nb}$ and $A_\parallel{}^{Nb}$ but negative values of $A_\perp{}^{Nb}$. The calculated spin densities (Table II) show that the relative contributions of 5s and 4d rise from ~1:9.2 for Nb(η-C_6H_6)$_2$ to ~1:7.7 for Nb(η-$C_6H_3Me_3$)$_2$.

Ta(η-C_6H_6)$_2$. The isotropic spectrum of Ta(η-C_6H_6)$_2$ shows considerably larger coupling to the metal (Table I) than for the vanadium or niobium complexes (^{181}Ta, I = $^7/_2$, 100%). The frozen solution spectrum is reminiscent of that of Nb(η-C_6D_6)$_2$ with $A_\parallel \gg A_\perp \gg A_H$, and proton hyperfine is detected only at the central feature where parallel and perpendicular bands are in near coincidence (Figure 4). The irregularities of the perpendicular features are again found to originate in second-order effects. The analysis reveals that $g_\perp$ is lower and $A_\parallel{}^{Ta}$ and A^H considerably higher than for the other metals (Table I). The value of $2B$ for Ta(η-C_6H_6)$_2$ is positive with all A components positive, implying a major 6s contribution to the spin density (6s:5d contributions 1:4.9, Table II).

PES. Ionization energy data and assignments are given in Table III, and representative spectra are shown in Figures 5–8.

The photoelectron spectra of all compounds show bands above 11 eV characteristic of their respective ligands. These are attributed to ionization of electrons associated with the lowest π level and the σ structure of the rings. Two bands, B and B′, occur between 8 and 11 eV which may be assigned to ionization of electrons from e_1 orbitals. Their relative intensity differ in the He I and He II spectra, the band at higher IE, B′, becoming more intense in the latter. This intensity increase may be associated with metal d content in the orbital from which the electron was ionized and so leads to assignment of B′ to the $^2E_{1g}$ ion state and B to the $^2E_{1u}$ ion state. The compounds M(η-C_5H_5)(η-C_6H_6) lack a center of inversion so the e_1 levels are not so rigorously classified, but again the higher ionization energy band B′ is relatively more intense in the He II spectrum implying a higher d content for its associated orbital.

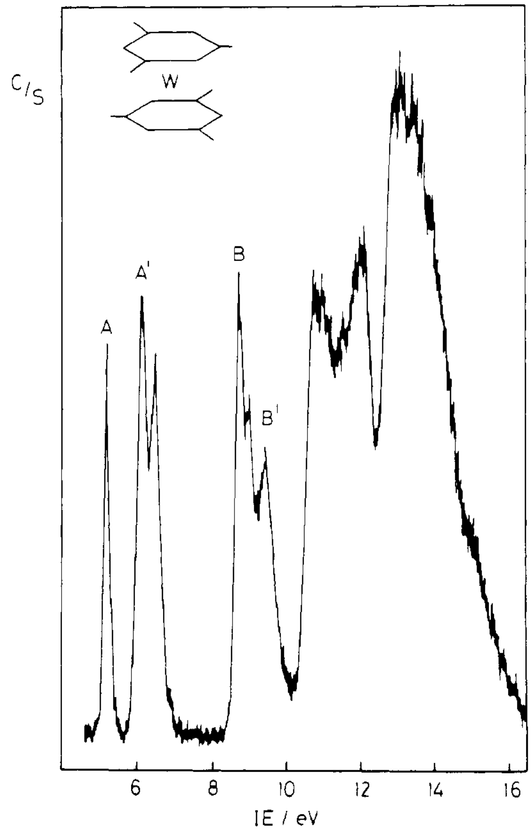


Figure 5. He I photoelectron spectrum of W(η-$C_6H_3Me_3$)$_2$. For meaning of labels, see text and Table III.

Below 8 eV bands are found characteristic of the d^n configuration of the complex.

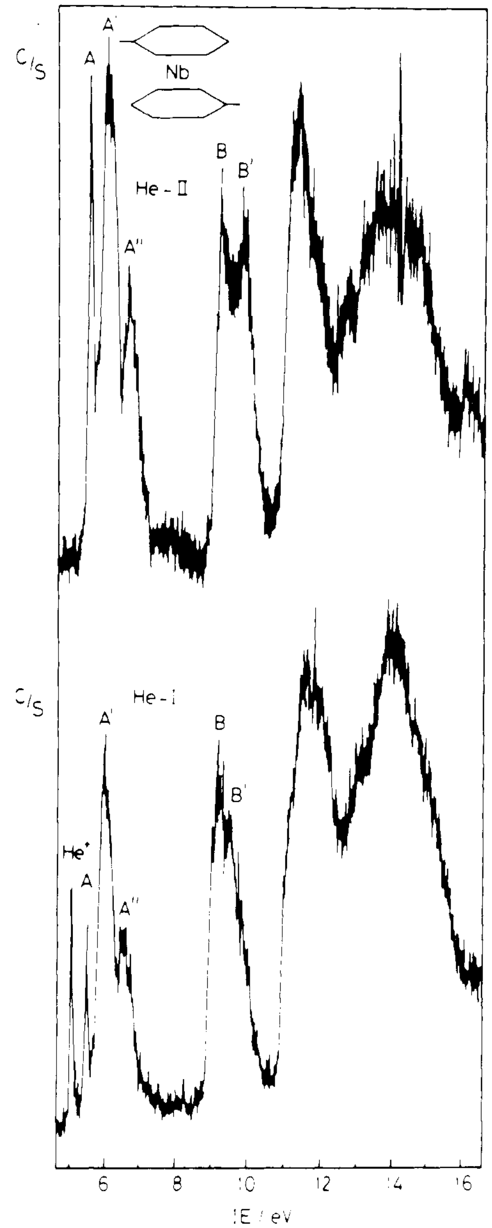


Figure 6. He I and He II photoelectron spectra of Nb(η-$C_6H_5Me)_2$. The low energy band marked He^+ is due to ionization of He gas diffusing from the lamp by He II radiation.

d⁶ Compounds. The group 6 compounds have the ground-state configuration $e_2^4a_1^2$. For tungsten this gives rise to three bands in the photoelectron spectrum, a sharp low-energy band assignable to the $^2A_1$ ion ground state, and two broader bands at higher IE due to $^2E_{5/2}$ and $^2E_{3/2}$ ion states (Figure 5). The spin–orbit coupling constant of tungsten is sufficiently large for these spin–orbit states to be resolved. For pure d ion states the splitting would be predicted as $2\zeta = 0.64$ eV.[19] The lower values found in the bis(arene)tungsten compounds (the measured values of 2ζ for W(η-arene)₂ are, (η-C_6H_6), 0.43, (η-C_6H_5Me), 0.37, and, (η-$C_6H_3Me_3$), 0.35 eV) suggest that the e_2 electrons are delocalized onto the ligands.

d⁵ Compounds. The vanadium and niobium compounds have a ground-state configuration $e_2^4a_1^1$. On ionization this gives rise to three ion states $^1A_1$, $^3E_2$, and $^1E_2$. The vanadium compounds show similar spectra to V(η-$C_6H_3Me_3)_2$ with a broad first ionization with a sharp high-energy shoulder and a broader, weaker band at about

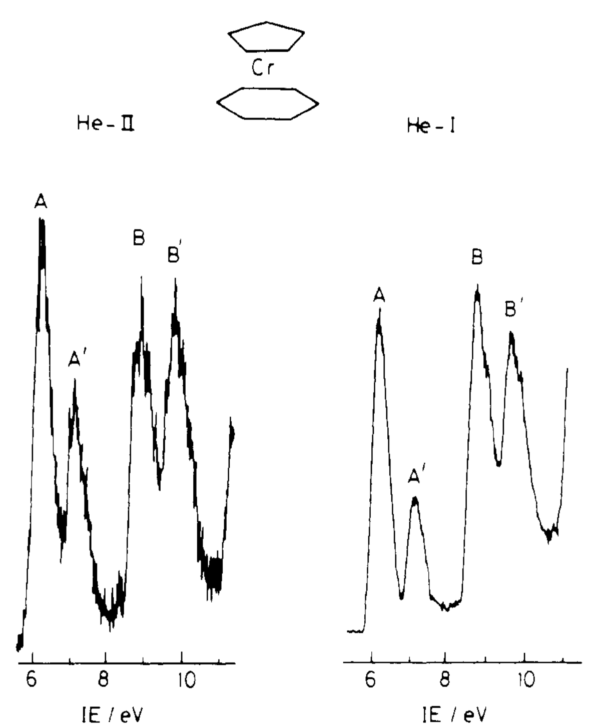


Figure 7. He I and He II photoelectron spectra of Cr(η-C_6H_6)(η-C_5H_5).

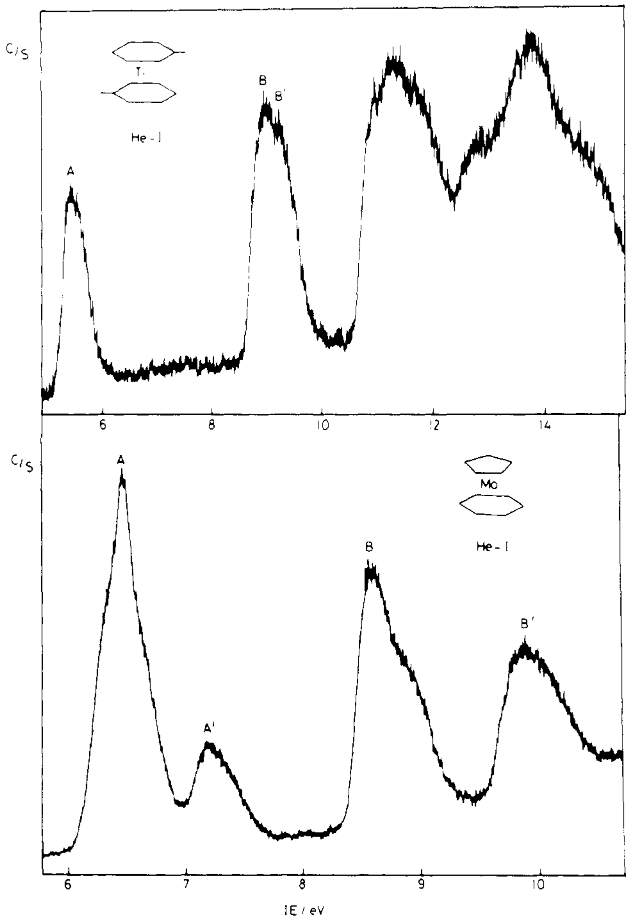


Figure 8. Above: He I photoelectron spectrum of Ti(η-$C_6H_5Me)_2$. Below: He I photoelectron spectrum of Mo(η-C_6H_6)(η-C_5H_5). Note change of IE scale.

---

[19] Griffith, J. S. "The Theory of Transition-Metal Ions", Cambridge University Press: Cambridge, 1961.

Table III. Ionization Energies (eV) and Measurement Conditions of Metal Arene Complexes

d^6 Compounds

assignt	$W(\eta\text{-}C_6H_6)_2$	$W(\eta\text{-}C_6H_5Me)_2$	$W(\eta\text{-}C_6H_3Me_3)_2$	label
$^2A_1$	5.40	5.25	5.18	A
$^2E_{5/2}$	6.56	6.28	6.16	A′
$^2E_{3/2}$	6.99	6.65	6.51	A″
$^2E_{1u}$	9.58	9.32	8.77	B
		9.59	9.06	
$^2E_{1g}$	10.3	10.08	9.48	B′
ligand bands	11.9	11.5	10.8	
	14.5	14.0	12.0	
	17.4	16.3	13.1	
measurement conditions[a]	90° 600 c/s	94° 1000 c/s	90° 400 c/s	He I
	105° 40 c/s	100° 100 c/s	100° 100 c/s	He II

d^5 Compounds

assignt	$V(\eta\text{-}C_6H_6)_2$	$V(\eta\text{-}C_6H_5Me)_2$	label
$^3E_2$	5.95	5.82	A′
$^1A_1$	6.10	5.99	A
$^1E_2$	6.70	6.56	A″
e_{1u}	9.46	9.35	B
e_{1g}		9.62	B′
ligand bands	11.3	11.3	
	12.0	13.0	
	13.9	14.1	
	14.9	14.7	
	16.4	15.7	
measurement conditions[a]	125° 1000 c/s	86° 550 c/s	He I

assignt	$Nb(\eta\text{-}C_6H_6)_2$	$Nb(\eta\text{-}C_6H_5Me)_2$	$Nb(\eta\text{-}C_6H_3Me_3)_2$	label
$^1A_1$	5.6	5.43	5.18	A
$^3E_2$	6.2	5.90	5.59	A′
$^1E_2$	6.7	6.46	6.15	A″
e_{1u}		9.14	8.59	B
e_{1g}		9.46	9.19	B′
ligand bands		12.9	11.0	
		15.3	11.5	
		17.7	12.1	
			13.4	
measurement conditions[a]	120° 100 c/s	85° 350 c/s	100° 3000 c/s	He I
		86° 80 c/s	100° 100 c/s	He II

assignt	$Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$	assignt	$Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$	label
$^3E_2$	6.20	$^3E_2 + {}^1A_1$	6.46	A
$^1E_2 + {}^1A_1$	7.15	$^1E_2$	7.25	A′
e_1	8.76	e_1	8.68	B
	9.17		8.93	
e_1	9.68	e_1	9.89	B′
ligand bands	11.5	ligand bands	11.4	
	12.1		12.1	
	13.9		13.8	
	17.1		16.8	
measurement conditions[a]	75° 1000 c/s		52° 1000 c/s	He I
	80° 130 c/s			He II

d^4 Compounds

assignt	$Ti(\eta\text{-}C_6H_6)_2$	$Ti(\eta\text{-}C_6H_5Me)_2$	
$^2E_2$	5.5–6.0	5.4	
$^2E_{1u}$		9.0	
$^2E_{1g}$		9.3	
ligand bands		11.2	
		13.8	
measurement conditions[a]	70° 500 c/s	60° 800 c/s	He I

[a] Measurement conditions are given in °C and counts s^{-1}.

6.5 eV.[14] The ion ground state is therefore assigned as $^3E_2$ followed by $^1A_1$ and $^1E_2$ at higher energy. The spectra of the bis(arene)niobium compounds show a sharp first ionization band which on comparison of the He I and He II spectra has the intensity characteristics of ionization from an a_1 orbital and is thus assigned to the $^1A_1$ ion state (Figure 6). The two subsequent bands are broader and have intensity ratios of approximately 3:1 and are thus assigned to the $^3E_2$ and $^1E_2$ ion states.

The compounds $M(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$ show only two bands in the d region. In the case of $Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$, whose He I spectrum has been reported previously, it was first assumed on intensity grounds that the first band comprised both the $^3E_2$ and the $^1A_1$ ionizations. However, further considerations of energy trends led to a reassignment such that the $^1A_1$ lay with the $^1E_2$ ionization in the second band. We have measured the He II spectrum of this compound and shown that the second band undergoes the greater intensity increase on increasing the photon energy (Figure 7). As ionizations from a_1 orbitals show a greater He II/He I intensity ratio, the second of these two assignments is confirmed as indicated in Table III. In contrast it is clear from the profile of the first band in the spectrum of Mo(η-C_5H_5)(η-C_6H_6) that it is composite in nature, the sharp profile of the $^1A_1$ ionization band being superimposed on the broader $^3E_2$ ionization band (see Figure 8).

d^4 Compounds. The two titanium compounds show a broad band with IE < 6 eV (Figure 8). This may be assigned to the ionization of a molecular $e_2{}^4$ configuration to a $^2E_2$ ion ground state. The molecular ground state differs from that of the isoelectronic chromocene[4] which has the configuration $e_2{}^3a_1{}^1$.

Discussion

The possible electron configurations of the bis(η-arene)metal complexes in their ground states were summarized in Scheme I. Diagrams of the orbitals involved in major interactions between arene and metal are shown in the orbital diagrams of Figure 9a. The extent of the a_{1g} interactions of the metal nd_{z^2} and $(n + 1)$s orbitals with the ligands is limited because the nodal cone of the d_{z^2} orbital intersects the closest lobes of the carbon $2p_\pi$ orbitals and approaches close to the hydrogens (Figure 9b).

ESR Spectra. The spectra of all the d^5 bis(arene)metal complexes are axial with $g_\parallel \simeq 2$ and $g_\perp < 2$ in accord with a $^2A_1$, $e_2{}^4a_1{}^1$ configuration. The increases in $(g_e - g_\perp)$ down the group ($-\Delta g_\perp$ = 0.0163 (V(η-C_6H_6)$_2$), 0.0203 (Nb(η-C_6H_6)$_2$), 0.0603 (Ta(η-C_6H_6)$_2$)) are small in relation to the increases in spin–orbit coupling constant (ζ(V): ζ(Nb): ζ(Ta) = 1:3:10.5),[19] implying large increases in Δ_1 in the second- and third-row transition-metal complexes (eq 1). There is a marked change in appearance of the spectra from V ($A_\perp \gg A_\parallel \simeq A^H$) to Nb ($A_\parallel \gg A_\perp \geq A^H$) to Ta ($A_\perp \gg A_\perp \gg A^H$). The analysis demonstrates that this change originates in appreciable $nd/(n + 1)$s mixing in the Nb and Ta complexes, which is absent from vanadium complexes (Table II). Thus the values of A_{iso} follow the trend V(η-arene)$_2$ < 0 < Nb(η-C_6H_6)$_2$ < Nb(η-C_6H_5Me)$_2$ < Nb(η-$C_6H_3Me_3$)$_2$ < Ta(η-C_6H_6)$_2$. This increase in s character must originate in improved mixing between the metal and arene a_1 orbitals.

The extent of delocalization onto the rings is most effectively estimated from A^H, since the d-electron populations rest on estimates of $2B°$. There is a marked increase in A^H on descending the group with smaller increases in ring substitution in the niobium complexes. If Drago's explanation of the proton couplings[7] (see Introduction) is applicable to the heavier metals, as seems likely, the extent of delocalization must increase down the group and the total proton spin density in Ta(η-C_6H_6)$_2$ may be as high as 14%. This increase must be associated with higher values of Δ_1 and the improved overlap of the heavier metals. Although the proton spin density does not increase appreciably with methyl substitution of the niobium complexes, there are significant increases in the $(n + 1)$s electron density. This may be taken to indicate slight improvements in overlap in the substituted arene complexes.

PES. The weight of the evidence from the PE studies of metal arene complexes indicates that there is back-bonding from the metal to the ligand via the e_2 orbitals (a linear combination of the metal $d_{x^2-y^2}$ and d_{xy} orbitals and the ring e_2 orbitals) but that the a_{1g} orbital is largely nonbonding, consisting almost entirely of metal d_{z^2} character. These conclusions are supported by theoretical studies on bis(arene) compounds.[20] From our study we may cite three pieces of evidence in support of this claim. First, ligand field analysis (see below) of the ion states shows that Δ_2, the ligand field splitting of the e_2 and a_1 orbitals, is positive in all cases: that is the e_2 orbital lies *below* the a_1 orbital. In the cases of the d^4 compounds the fact that the ground-state configuration is $e_2{}^4$ provides similar evidence. Second, the band widths for the e_2 ionization bands are ca. 0.5 eV, indicating bonding character, whereas those of the a_1 ionizations are unusually narrow for molecules of this size (ca. 0.15 eV), indicating nonbonding character. Thirdly the spin–orbit splitting of the $^2E_{5/2}$ and $^2E_{3/2}$ ion states for the bis(arene)tungsten cations is reduced compared with the value for free W^+, indicating delocalization of these electrons onto the ligand.

In principle we now have sufficient data to enable comparison of the bonding of arenes to different metals. To

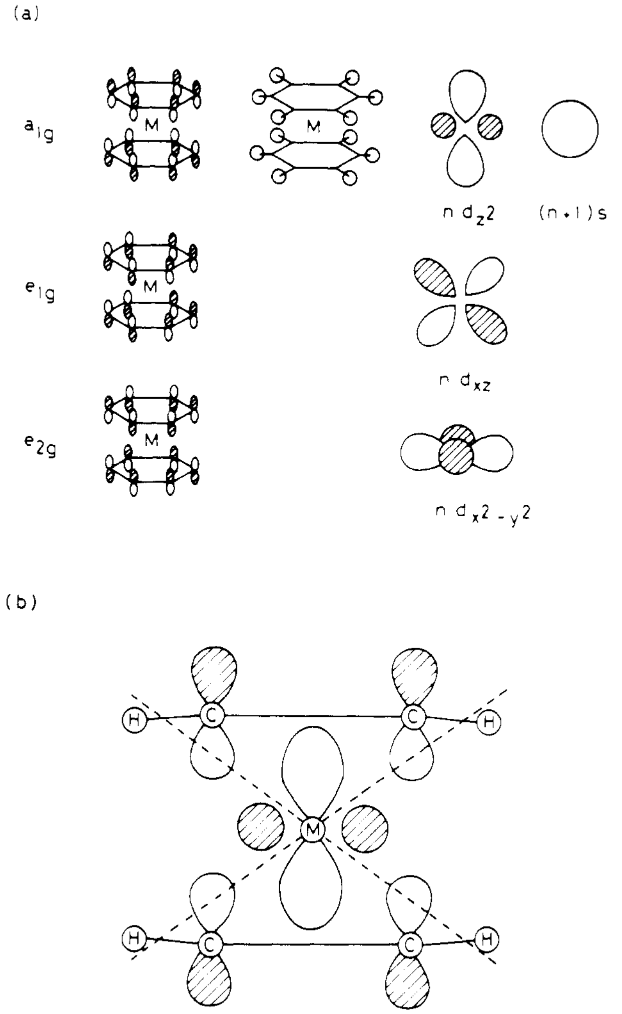


Figure 9. (a) Diagrams showing the potential interactions of ligand and metal *n*d, $(n + 1)$s metal orbitals. (b) Diagram showing the intersection of the nodal cone of the d_{z^2} orbital with the ligand orbitals. The diagram is based on the geometry of Cr(η-C_6H_6)$_2$ deduced by electron diffraction (Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41).

---

(20) Weber, J.; Geoffroy, M.; Goursot, A.; Penigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995.

Table IV. Ligand Field Analysis of the Bis(arene)metal Cations[a]

16-electron cations				17-electron cations			
complex	Δ_2	B	β	complex	Δ_2	B	β
$[V(\eta\text{-}C_6H_6)_2]^+$	1.91	0.047	0.63	$[Cr(\eta\text{-}C_6H_6)_2]^+$	2.05	0.052	0.64
$[V(\eta\text{-}C_6H_5Me)_2]^+$	1.87	0.046	0.63	$[Cr(\eta\text{-}C_6H_5Me)_2]^+$	1.97	0.051	0.63
$[V(\eta\text{-}C_6H_3Me_3)_2]^+$	1.78	0.047	0.64	$[Cr(\eta\text{-}C_6H_3Me_3)_2]^+$	1.91	0.052	0.64
$[Nb(\eta\text{-}C_6H_6)_2]^+$	2.14	0.031	0.57	$[Mo(\eta\text{-}C_6H_6)_2]^+$	1.71	0.032	0.57
$[Nb(\eta\text{-}C_6H_5Me)_2]^+$	2.01	0.035	0.66	$[Mo(\eta\text{-}C_6H_5Me)_2]^+$	1.76	0.038	0.66
$[Nb(\eta\text{-}C_6H_3Me_3)_2]^+$	1.95	0.035	0.66	$[Mo(\eta\text{-}C_6H_3Me_3)_2]^+$	1.65	0.038	0.66
$[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$	1.66	0.059	0.73				
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$	2.17	0.049	0.88				

[a] Values for $B_{\text{free ion}}$ from: Jorgensen, C. K. *Helv. Chim. Acta* **1967**, 131. The calculations were performed using the equations and method given in the text. Data from ref 12–14 for the complexes whose PE spectra are not reported in this study.

facilitate understanding of the underlying causes of trends, we have carried out a ligand field analysis of the ion states using the expressions given below.[4] The e_2/a_1 splitting is given by functions of Δ_2 (see Scheme I), B and C. The Racah parameters, B and C, are measures of electron repulsion within the d shell. In deriving these expressions, we have assumed that $C = 4B$.

d^4 cations

$$E(^1A_1) = 56B \qquad E(^3E_2) = \Delta_2 + 12B$$

$$E(^1E_2) = \Delta_2 + 28B$$

d^5 cations

$$E(^2A_1) = 2\Delta_2 + 20B \qquad E(^2E_2) = \Delta_2 + 40B$$

For the d^5 compounds, where three ion states are observed, we can obtain values for both Δ_2 and B; we then use these B values to obtain the nephelauxetic ratio, β, for the group 5 metal. We assume the same value of β for the adjacent group 6 metal, which in turn leads to a value of B. A value for Δ_2 may then be calculated in the group 6 case. Results obtained are given in Table IV.

On passing from a first- to a second-row metal, there is a significant drop in the electron–electron repulsion parameter B. This is responsible for various contrasts between the spectra of the first- and second-row congeners. Most strikingly the difference in ground state for $[V(\eta\text{-arene})_2]^+$ $(^3E_2)$ and $[Nb(\eta\text{-arene})_2]^+$ $(^1A_1)$ is attributable to a combination of the lower exchange energy and the larger ligand field splitting in the second-row complex. Also on passing from a d^5 to a d^6 system, there is a large decrease in the a_1 ionization energy in the first row but little in the second row, as a result of the smaller B values. The fact that the $^2A_1 - {^2E_2}$ splitting is almost constant for the group 6 metal bis(arene) cations is seen to be a balance of a decrease in Δ_2 and a decrease in B on going down the group. This *decrease* in Δ_2 between $[Cr(\eta\text{-arene})_2]^+$ and $[Mo(\eta\text{-arene})_2]^+$ is in contrast to the *increase* found between $[V(\eta\text{-arene})_2]^+$ and $[Nb(\eta\text{-arene})_2]^+$ and the *increase* found between $[Cr(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ and $[Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$.

Methyl substitution on the arene ring appears to decrease Δ_2, presumably as the ring becomes a worse acceptor of the metal electrons. The data on $[Mo(\eta\text{-}C_6H_6)_2]^+$ appear to contradict this trend, but it should be noted that this value is dependent on the B value deduced for $[Nb(\eta\text{-}C_6H_6)_2]^+$, where measurement conditions were far from ideal and so the data are subject to greater error.

The separation of the e_{1u} and e_{1g} ionization bands is significantly greater for the molybdenum bis(arene) and tungsten bis(arene) compounds than for the chromium bis(arene) compounds (Cr 0.4, Mo 0.7, W 0.7 eV). Greater delocalization for the second- and third-row transition metals is the probable cause, the e_{1g} interaction being the principal ligand-to-metal donor interaction.

Conclusions

The bis(η-arene)metal complexes provide a unique series of stable, isostructural, closed-shell, and open-shell molecules and ions, inviting comparisons between different metals and electron configurations. The PE spectra offer a general probe of electron configuration and orbital energies. They are a source of important evidence for the back-bonding characteristics of the highest occupied e_2 levels and also provide an estimate for Δ_2 for the cations. To the photoelectron "eye" the highest occupied a_1 levels appear nonbonding. The ESR spectra, where applicable, probe the electronic structure in a complementary way. They allow unambiguous assignment of the ground state and are particularly sensitive to the detailed composition of the a_1 SOMO. They also provide an indication of trends in Δ_1. The increased overlap down the group is indicated by the e_{1g}/e_{1u} splittings in the PE spectra, by the proton and $(n + 1)$s electron densities, and by the increasing values of Δ_1 found by ESR. While the magnitude of Δ_2 follows these trends for the d^4 cations, Δ_2 decreases from Cr to Mo for the d^5 cations.

Finally, we may comment on the remarkable stability of the d^5 $M(\eta\text{-arene})_2$ radicals. Like $V(CO)_6$, they are stable to dimerization and hydrogen atom abstraction from hydrocarbons, but unlike the latter complex they are not readily reduced to the anion.[21] (The $V(\eta\text{-arene})_2$ complexes may be reduced on a potassium film,[22] but this technique does not work for the niobium and tantalum analogues.) In contrast, the $5d^5$ complex $Re(\eta\text{-}C_5H_5)_2$ probably does abstract H atoms readily and can be stabilized only in a low-temperature matrix.[23] Since the bent bis(η-arene)metal complexes $[W(\eta\text{-arene})_2H]^+$ and $Hf(\eta\text{-arene})_2(PMe_3)$ are stable,[2,24] it would be unreasonable to attribute the stability of $M(\eta\text{-arene})_2$ (M = Nb,Ta) to steric factors alone. In this context, we note that bending converts the a_1 SOMO into a new a_1 hybrid orbital ideal for bonding to an additional ligand.[25] The ESR spectra show increasing delocalization of this electron down the group of $M(\eta\text{-arene})_2$ complexes, suggesting that there may be a substantial reorganization energy opposing the bending. With regard to electron addition to $M(\eta\text{-arene})_2$, we note

---

(21) Bratt, S. W.; Kassyk, A.; Perutz, R. N.; Symons, M. C. R. *J. Am. Chem. Soc.* **1982**, *104*, 490.

(22) Elschenbroich, C.; Gerson, F. *J. Am. Chem. Soc.* **1975**, *97*, 3556.

(23) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1981**, 452. Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N.; Powell, M. H. A. *Inorg. Chem.* **1983**, *22*, 1675.

(24) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 127.

(25) Evans, S.; Green, J. C.; Orchard, A. F.; Saito, T.; Turner, D. W. *Chem. Phys. Lett.* **1969**, *4*, 361.

that PE spectra indicate that any extra electron would be very weakly bound. The ionization energies of the neutral species are only about 5.5 eV, and there is a substantial electron repulsion term disfavoring electron addition. In contrast the first PE band of $V(CO)_6$ appears at 7.5 eV,[26] and the electrons are probably more delocalized. Additionally, electroneutrality considerations suggest that it will be much easier to form the anions with a better π acceptor such as CO.

Acknowledgment. We are grateful to Dr. J. B. Raynor for providing the ESR simulation program and to Prof. M. C. R. Symons for helpful discussions. We also acknowledge Balliol College, Oxford, for support (F.G.N.C.) and SERC for equipment.

Note Added in Proof. It has recently proved possible to isolate the 17-electron complexes $[Ti(\eta\text{-}C_6H_6)_2]^-$ and $[Ti(\eta\text{-}C_6H_5Me)_2]^-$ as their potassium salts by reduction of the $Ti(\eta\text{-arene})_2$ with potassium or KH. Their ESR spectra show proton hyperfine coupling with $A^H = 4.6$ G for $[Ti(\eta\text{-}C_6H_6)_2]^-$ and $A^H = 4.5$ G for $[Ti(\eta\text{-}C_6H_5Me)_2]^-$. These data indicate substantial increases in delocalization across the isoelectronic series $[Cr(\eta\text{-}C_6H_6)_2]^+$ ($A^H = 3.5$ G), $V(\eta\text{-}C_6H_6)_2$ ($A^H = 4.1$ G), and $[Ti(C_6H_6)_2]^-$ ($A^H = 4.6$ G) (Berry, A.; Green, M. L. H.; Perutz, R. N., to be submitted for publication).

Registry No. $V(\eta\text{-}C_6H_6)_2$, 12129-72-5; $V(\eta\text{-}C_6H_5Me)_2$, 12131-27-0; $Nb(\eta\text{-}C_6H_6)_2$, 68088-94-8; $Nb(\eta\text{-}C_6D_6)_2$, 86119-97-3; $Nb(\eta\text{-}C_6H_5Me)_2$, 68088-95-9; $Nb(\eta\text{-}C_6H_3Me_3)_2$, 68088-96-0; $Ta(\eta\text{-}C_6H_6)_2$, 80346-26-5; $W(\eta\text{-}C_6H_6)_2$, 12089-23-5; $W(\eta\text{-}C_6H_5Me)_2$, 52346-44-8; $W(\eta\text{-}C_6H_3Me_3)_2$, 67087-69-8; $Cr(\eta^5\text{-}C_5H_5)(\eta\text{-}C_6H_6)$, 12093-16-2; $Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$, 12153-25-2; $Ti(\eta\text{-}C_6H_6)_2$, 52462-43-8; $Ti(\eta\text{-}C_6H_5Me)_2$, 55527-82-7; $V(\eta\text{-}C_6H_3Me_3)_2{}^+$, 86119-98-4.

---

[26] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Bashkin, J. K. D. Phil. Thesis, University of Oxford, 1982.

(η^3-Allyl)dicarbonylmolybdenum(II) Complexes: Studies of Their Redox Chemistry and Solution Equilibria by Electrochemistry

Brian J. Brisdon,[1a] Kay A. Conner,[1b] and Richard A. Walton*[1b]

School of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom, and the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received January 4, 1983

Electrochemical oxidation of the complexes $(\eta^3\text{-}RC_3H_4)Mo(CO)_2(L\text{–}L)X$ (where R = H or CH_3, L–L = 2,2′-bipyridyl when X = Cl or O_2CCF_3 and L–L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or $Ph_2AsCH_2CH_2AsPh_2$ when X = Cl) in dichloromethane–0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) solutions generates the ESR active 17-electron cations $[(\eta^3\text{-}RC_3H_4)Mo(CO)_2(L\text{–}L)X]^+$. Differences between the spectra of the complexes containing 2,2′-bipyridyl and the phosphine/arsine ligands can be attributed to structural differences that exist both between the neutral and the cationic species containing the N vs. P/As donors. The ionization of $(\eta^3\text{-}RC_3H_4)Mo(CO)_2(NCCH_3)_2Cl$ in dichloromethane–0.2 M TBAH, viz., $3(\eta^3\text{-}RC_3H_4)Mo(CO)_2(NCCH_3)_2Cl \rightleftharpoons [(\eta^3\text{-}RC_3H_4)Mo(CO)_2(NCCH_3)_3]^+ + [(\eta^3\text{-}RC_3H_4)_2Mo_2(CO)_4Cl_3]^- + 3CH_3CN$, can be followed by cyclic voltammetry through the characteristic electrochemical properties of the cation and anion. Whereas ionization in this solvent system is essentially complete, little ionization occurs in acetonitrile–0.1 M TBAH solutions.

Introduction

Reactions of the acetonitrile and alkyl isocyanide complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ and $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ with tertiary phosphines provides a route, through the reductive elimination of allyl chloride, to molybdenum(0) complexes of the types $Mo(CO)_2(CNR)_4$, $Mo(CO)_2(CNR)_2(PR_3)_2$, and $Mo(CO)_2(PR_3)_4$.[2–4] Our recent study[5] of the reversible intramolecular isomerization of $Mo(CO)_2(CNR)_4$ and $Mo(CO)_2(CNR)_2(PR_3)_2$ following their oxidation to the corresponding 17-electron cations had led us to explore the redox properties of the synthetic precursor complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2(L)_2Cl$ and $(\eta^3\text{-}C_3H_5)Mo(CO)_2(L\text{–}L)Cl$, where L is a monodentate donor and L–L a chelating bidentate. In the present report, we describe the electrochemical properties of this class of complexes which not only provide insight into the electronic structure of these species but, furthermore, are of relevance to the solution equilibria which may exist in nonaqueous solvents.[6,7]

Experimental Section

Starting Materials. The (η^3-allyl)dicarbonylmolybdenum(II) complexes and closely allied derivatives were prepared by standard literature procedures[2,6,8–11] as were the two tungsten derivatives $(\eta^3\text{-}C_3H_5)W(CO)_2(NCCH_3)_2Cl$ and $(\eta^3\text{-}C_3H_5)W(CO)_2(dppe)Cl$

---

[1] (a) University of Bath. (b) Purdue University.

[2] King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 74.

[3] Deaton, J. C.; Walton, R. A. *J. Organomet. Chem.* **1981**, *219*, 187.

[4] Brisdon, B. J.; Edwards, D. A.; Paddick, K. E. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 83 and references therein.

[5] Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 169.

[6] Brisdon, B. J.; Cartwright, M. *J. Organomet. Chem.* **1979**, *164*, 83.

[7] Drew, M. G. B.; Brisdon, B. J.; Cartwright, M. *Inorg. Chim. Acta* **1979**, *36*, 127.

[8] Brisdon, B. J.; Day, A. *J. Organomet. Chem.* **1981**, *221*, 279.

[9] Hull, C. A.; Stiddard, M. H. B. *J. Organomet. Chem.* **1967**, *9*, 519.

[10] Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, C1.

[11] Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865 and references cited therein.

0276-7333/83/2302-1159$01.50/0