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MONO- AND BI-NUCLEAR PENTACARBONYL COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN WITH THE ANION RADICALS OF 2,1,3-BENZOXADIAZOLE, 2,1,3-BENZOTHIADIAZOLE AND 2,1,3-BENZOSELENADIAZOLE

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Summary

Substitution reactions of metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) with the radical anions of 2,1,3-benzoxadiazole, 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole yield paramagnetic mono- and bi-nuclear metal pentacarbonyl complexes. The ligand-centered radicals were identified and studied in THF solution by electron spin resonance, Hückel MO calculations were employed to account for the spin redistribution in the radical ligands upon complexation. The mononuclear radical species display ambivalent, possibly fluxional, behaviour, which was not found to the same extent in the corresponding neutral complexes.

Recently, we have reported several mono- and bi-nuclear complexes of Group VIB metal carbonyls with radical anions of aromatic *N*-heterocycles [1–5]. These species were obtained in solution by alkali metal or electrochemical reduction and were studied by high resolution ESR spectroscopy. *N*-Heterocyclic anion radicals are very good complex ligands because of their overall negative charge, their strong σ coordination through the nitrogen lone pairs, and the possibility of π back bonding from an electron-rich metal into the singly occupied (= half empty) molecular orbital of the radical ligand. It was demonstrated that such radical complexes can undergo CO replacement by suitable ligands such as phosphanes and phosphites [3,5]. Furthermore, the existence of ligand-centered radical anion complexes indicates that the first electronically excited state of the neutral complex arises from a metal-to-ligand charge transfer [4,5].

So far, pure *N*-heterocycles such as pyridines, pyrimidines and pyrazines have been used as ligands in radical complexes of Group VIB metal carbonyls [2–5]. In this work we describe the use of some mixed heterocyclic systems, the 2,1,3-benzo-

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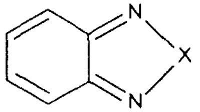
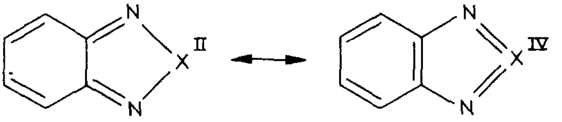
chalcogenadiazoles **1–3**, as substrates for the radical anion complexation.



(**1**, X = O;
2, X = S;
3, X = Se) (1)

Several reasons led us to choose this particular system: (i) Compounds **1–3** are easily obtained (cf. experimental section), and so the influence of various heteroatoms X may be studied.

(ii) For X = S, Se, two plausible resonance structures can be formulated (eq. 2); the *o*-quinonediimine arrangement **A** as well as the sulfur(IV) or selenium(IV) diimine system **B** can function as metal coordination site involving redox activity [6,7]:

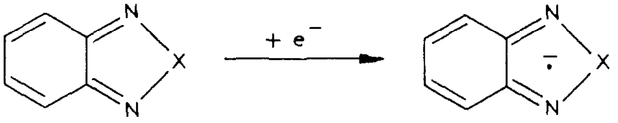


(2)

(**A**) (**B**)

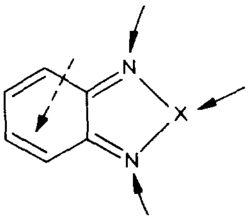
(X = S, Se)

(iii) Anion radicals of all the derivatives **1–3** are well known to be persistent, and several electrochemical and ESR studies have been reported [8,9]:



(3)

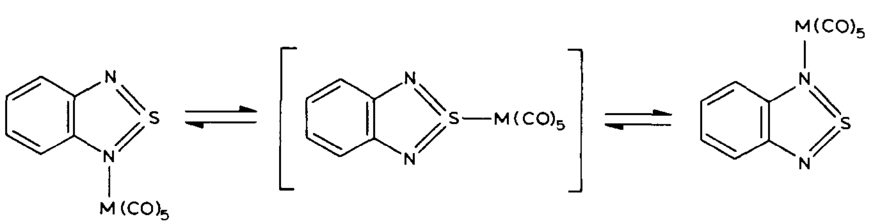
(iv) There are several potential coordination sites in systems such as **1–3**. Besides π-coordination, there is the possibility of single σ-coordination at N or X [10] or the coordination of two metal fragments at both nitrogen atoms (4):



(4)

Carbonyl complexes of a type **2** derivative were reported with 1/1 stoichiometry [11], and although the basicity of the second nitrogen atom is very low (**3**: $pK_1 = -1.41$, $pK_2 = -8.10$ [12]), the uptake of an electron is known to effectively increase the *N*-basicity in related systems such as the 1,4-diazines [13] or the 2,2′-bipyridines [14].

(v) Vrieze and coworkers [11] reported fluxional behaviour on the NMR time scale in 1/1 complexes of sulfurdiimines with pentacarbonyl metal fragments (eq. 5), this was explained by a gliding motion" of $M(CO)_5$ along the N=S=N system:

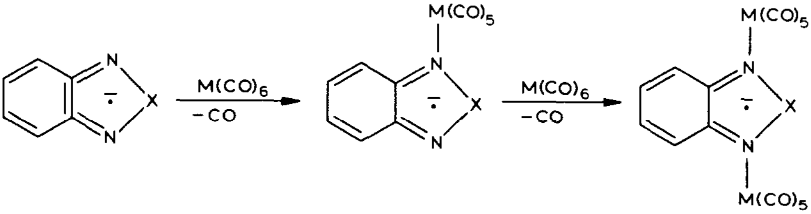


(5)

For all of these reasons we have studied the substitution reactions of the radical anions $\mathbf{1}^{\overline{\cdot}}$–$\mathbf{3}^{\overline{\cdot}}$ with Group VIB metal hexacarbonyls, identifying the species obtained by the ESR technique in solution. The results made it necessary to prepare the two neutral complexes $[\mathbf{2} \cdot W(CO)_2]$ and $[\mathbf{3} \cdot W(CO)_5]$ so that their ^1H NMR behaviour at variable temperature could be studied.

Results and discussion

Reactions of the radical anions $\mathbf{1}^{\overline{\cdot}}$–$\mathbf{3}^{\overline{\cdot}}$, generated by potassium reduction in THF, with excess metal hexacarbonyl of chromium, molybdenum or tungsten generally result in replacement of CO and the formation of first mono- and then bi-nuclear paramagnetic complexes (eq. 6).



(6)

In most cases, the reactions proceed quickly to yield the binuclear species, but the substitution rate is considerably lower for the combinations with the heavier elements, so that the formation of the binuclear Se/W complex is complete only after several months of reaction at room temperature.

The paramagnetic complexes are persistent in THF solution, and were identified and characterized by their ESR spectra (Fig. 1–4).

^1H and ^{14}N couplings from the heterocycle as well as metal isotope and, in two instances, ^{13}C splittings from CO groups are observed. Table 1 summarizes the coupling constants and g values as obtained from computer simulations of the spectra.

The spectral parameters of the binuclear species exhibit typical behaviour [2–4]: (i) The g value is increased for molybdenum and especially so for tungsten complexes because of the effect of the spin orbit coupling constant on g (contributions of excited states with non-zero angular moment [5]).

(ii) The ^{14}N splitting is approximately 25% higher in the complexes than in the free anion radical.

(iii) For a given ligand, metal isotope coupling constants show a relation $a_{^{183}W} > a_{^{95,97}Mo} > a_{^{53}Cr}$.

It is also interesting to compare the complexes of the three different ligands **1**, **2** and **3**. The series of the hyperfine coupling constants $a_{^{14}N}$, $a_{^{95,97}Mo}$ and $a_{^{183}W}$ demonstrate that the spin density at these centres is lowest for complexes of the sulfur ligand **2**. This may be attributed to a favourable spin delocalization onto the

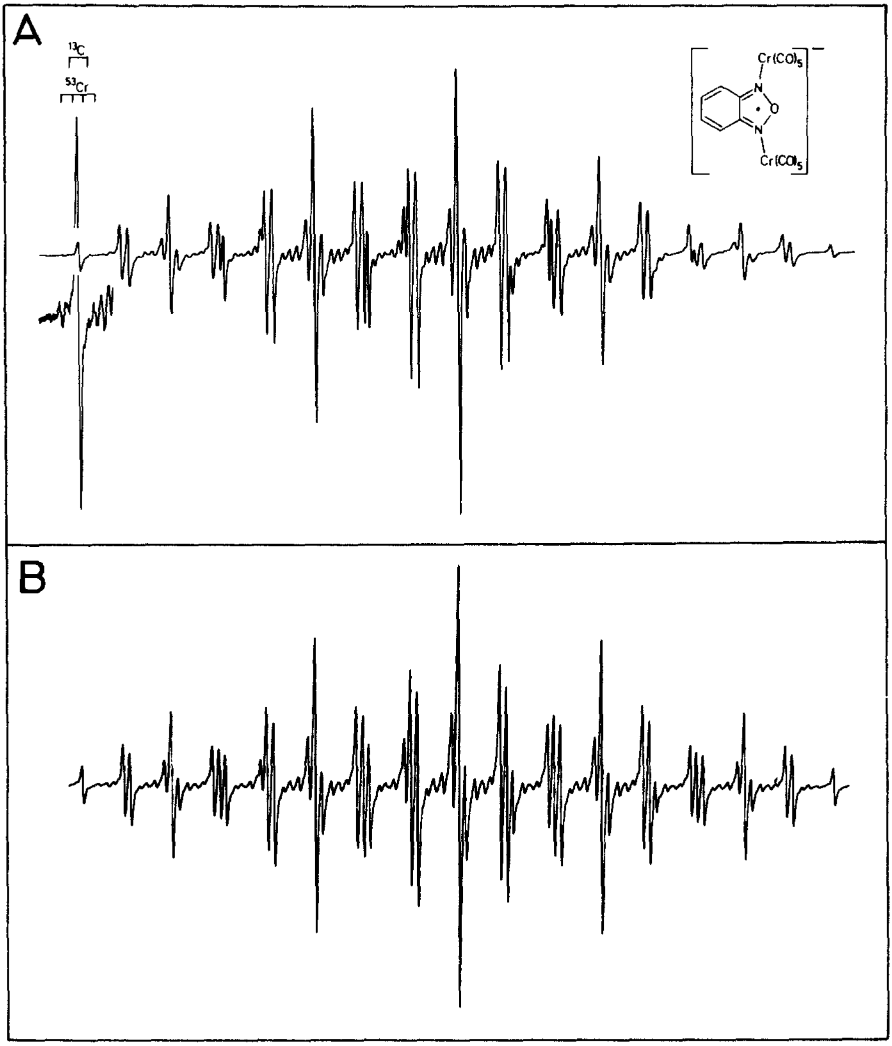


Fig. 1. (A) ESR spectrum of the radical complex $[\mathbf{1}\{Cr(CO)_5\}_2]^{-}$ K^+ at 300 K in THF, the amplified outermost line shows ^{13}C and ^{53}Cr isotope coupling. (B) Computer simulation with the data from Table 1 and a line width of 13 μT.

sulfur atom in such an arrangement, and is also in agreement with the large *g* values for the 2,1,3-benzothiadiazole radical complex, an effect of a strong contribution from resonance structure **B** (2).

The proton splittings in the organic part of the radical complexes indicate a substantial redistribution of spin upon complexation. For a given ligand, one splitting shows a considerable decrease on going from the free ligand radical anion via the chromium and molybdenum to the tungsten complex, whereas the other coupling constant hardly changes. For some binuclear complexes, this leads to an accidental degeneracy of both ^1H coupling constants (Table 1).

That peculiar behaviour of the proton couplings is, however, in complete agreement with the results from Hückel molecular orbital (MO) calculations (Fig. 5). The

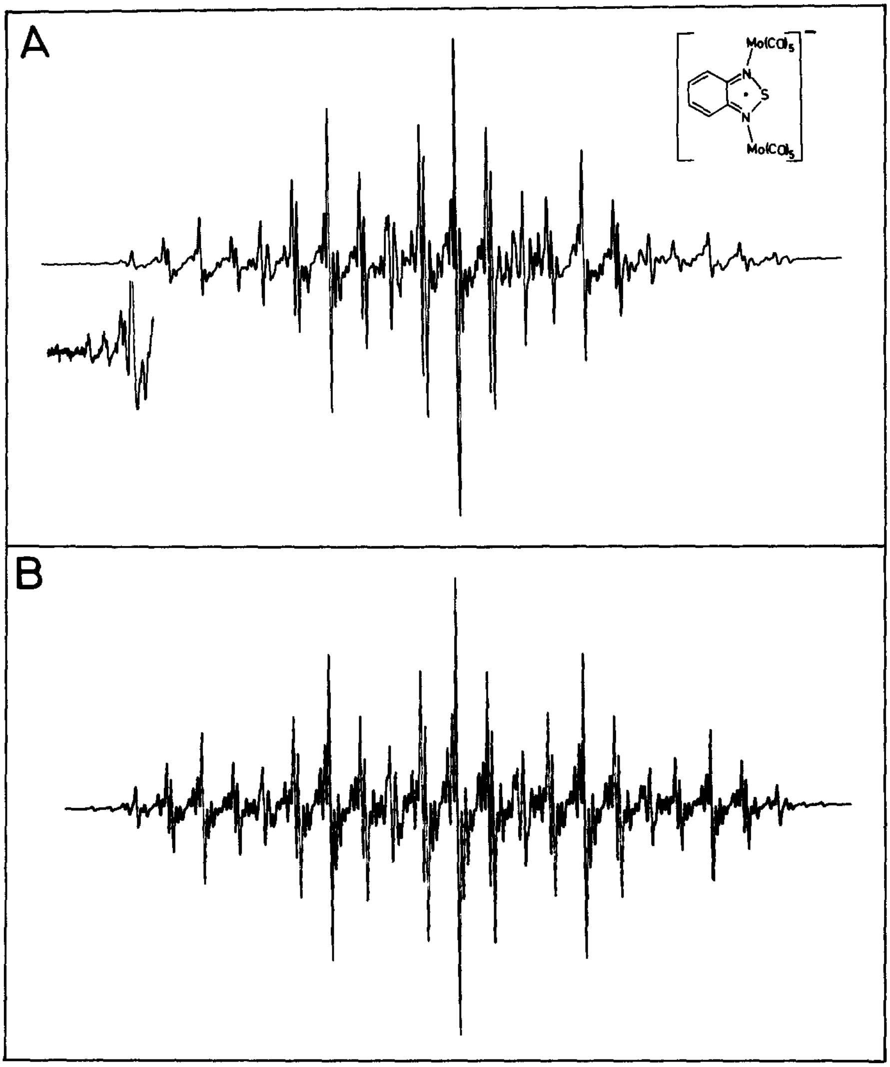
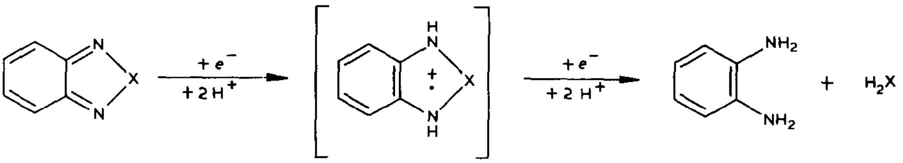


Fig. 2. (A) ESR spectrum of the radical complex $[2\{Mo(CO)_5\}_2]^{\cdot-}$ K^+ at 300 K in THF, the amplified wing section showing $^{95,97}Mo$ isotope coupling. (B) Computer assisted spectrum synthesis, line width 11 μT.

correlation of squared Hückel coefficients c_j^2 versus the nitrogen Coulomb integral parameter h_N reproduces the experimentally observed trends for $a_{H(4,7)}$ and $a_{H(5,6)}$ such as the accidental degeneracy at $h_N = 1.35$ (Fig. 5).

Incidentally, the strong increase of c_X^2 with increase in $h(N)$ illustrates that strong perturbation, such as the protonation of the anion radical, leads to irreversible extrusion of H_2X [15,16]:



(7)

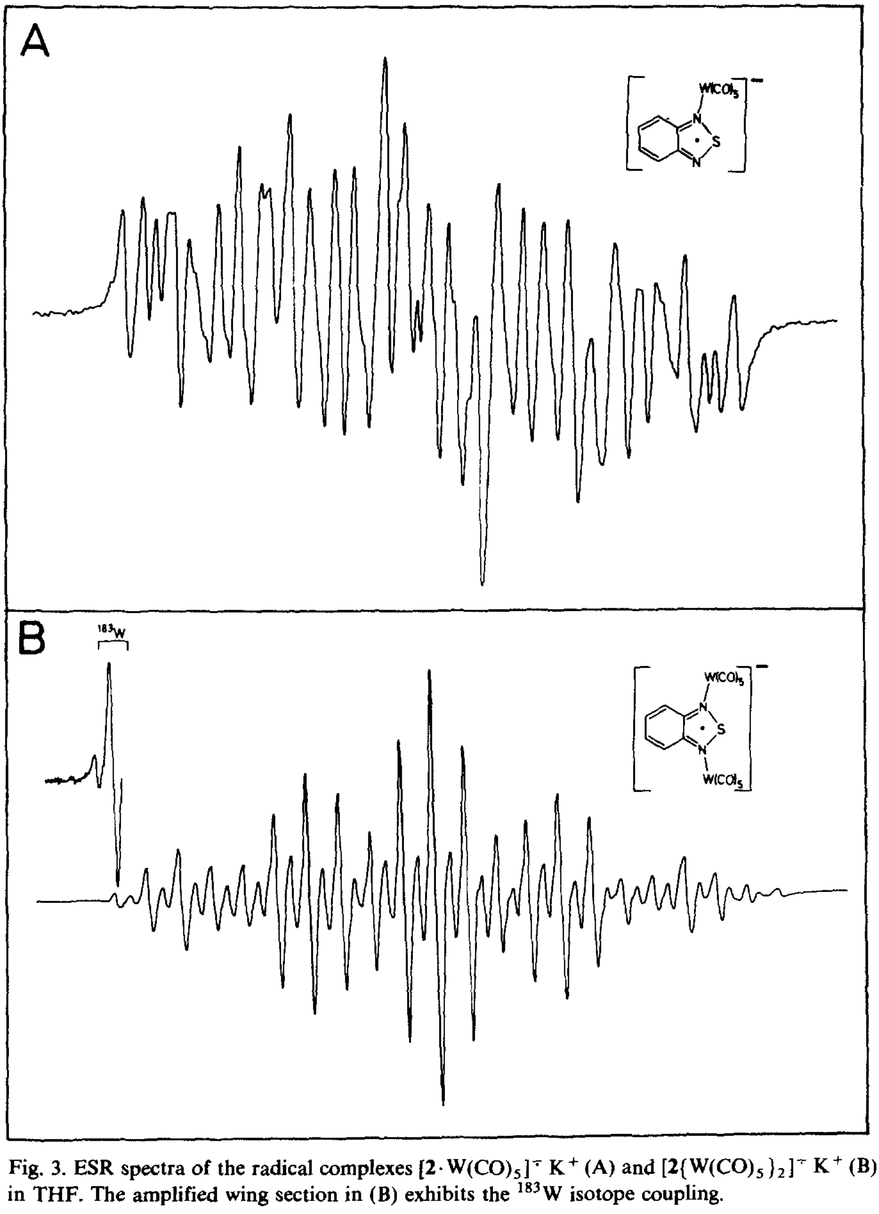


Fig. 3. ESR spectra of the radical complexes $[2 \cdot W(CO)_5]^{-\cdot}$ K^+ (A) and $[2\{W(CO)_5\}_2]^{-\cdot}$ K^+ (B) at 300 K in THF. The amplified wing section in (B) exhibits the ^{183}W isotope coupling.

When analyzing the mononuclear radical complexes which could, in a few instances, (Table 1) be observed long enough for ESR analysis, we found a remarkable dichotomy: most of the mononuclear complexes show an ESR spectrum (cf. Fig. 3A) clearly indicating asymmetry, i.e. coordination at one of the nitrogen atoms on the ESR time scale (10^{-6}–10^{-8} s). This asymmetry is indicated by the absence of a dominant central line (Fig. 3A), which proves that there is at least one set with an odd number of equivalent nuclei of non-integral nuclear spin. In contrast, the complex $[3 \cdot W(CO)_5]^{-\cdot}$ displays a spectrum whose splitting pattern

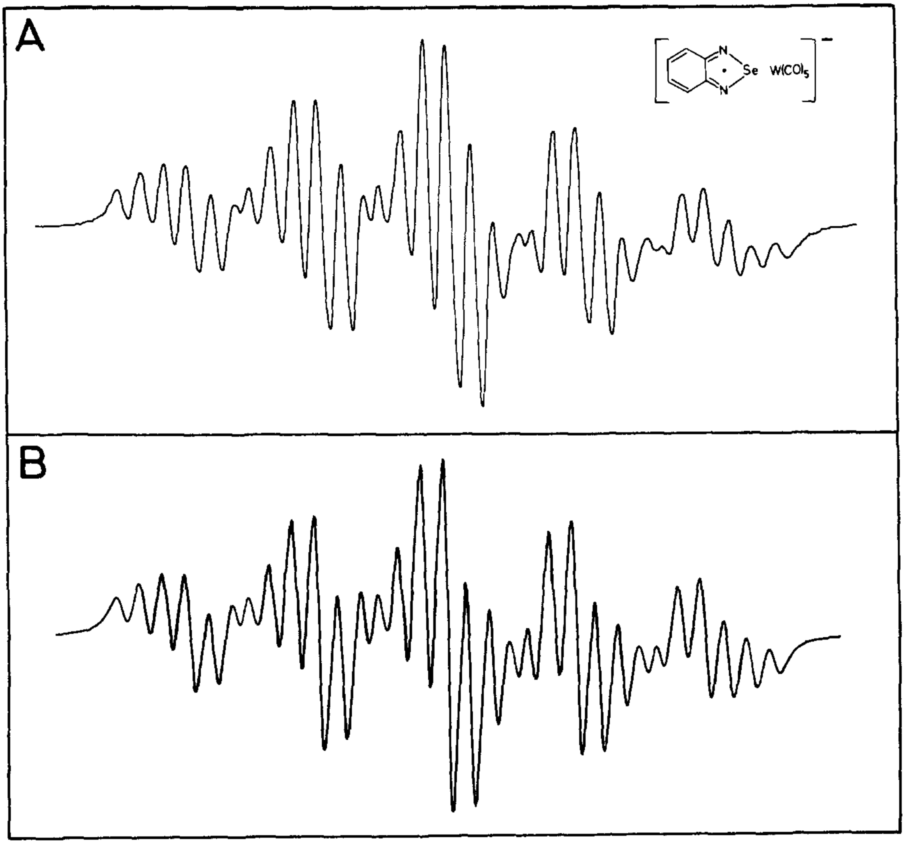


Fig. 4. (A) ESR spectrum of the radical complex $[\mathbf{3}\cdot W(CO)_5]^{\overline{\cdot}}$ K^+ at 300 K in THF. (B) Computer simulation with the coupling constants from Table 1 and a line width of 75 μT.

suggests C_{2v} symmetry (Fig. 4). The question arises whether this is a complex with coordination at selenium or a complex where rapid fluctuation of the metal carbonyl fragment occurs between the two nitrogen sites (eq. 5).

Vrieze and coworkers [11] have described both phenomena for neutral sulfurdiimine complexes, and they suggested that a structure with bonding of the heteroatom X to $M(CO)_5$ might be an intermediate in an N–N′ fluctuation process (eq. 5). Our attempts to freeze out an asymmetrical configuration of the radical complex $[\mathbf{3}\cdot W(CO)_5]^{\overline{\cdot}}$ were hampered below 0°C because of the typical anisotropic line broadening effects [2–5]. The redistribution of spin indicated by the ^1H coupling constants does not suggest a coordination at nitrogen, but the magnitude of $a(^{14}N)$ which is the average of the values $a(N)$ for the free radical anion and for the binuclear complex, points instead to N coordination of $W(CO)_5$ (Table 1). The latter alternative would, however, imply a very low barrier for the fluctuation process between the two nitrogen coordination sites (eq. 5).

Because of the obvious difference between the radical complexes $[\mathbf{2}\cdot W(CO)_5]^{\overline{\cdot}}$ (Fig. 3) and $[\mathbf{3}\cdot W(CO)_5]^{\overline{\cdot}}$ (Fig. 4) we also studied the variable temperature ^1H NMR spectra of the corresponding neutral complexes. Although broadening of the

TABLE 1

ESR PARAMETERS OF RADICAL LIGANDS AND COMPLEXES [a]

Radical	$a_{H(4,7)}$	$a_{H(5,6)}$	a_N	a_M [b]	g
$\mathbf{1}^{\cdot-}$ [8]	351	218	561	/	[c]
$[\mathbf{1}\{Cr(CO)_5\}_2]^{\cdot-}$	243	206	712	56 [f]	2.0042
$[\mathbf{1}\{Mo(CO)_5\}_2]^{\cdot-}$	245	206	713	124	2.0045
$[\mathbf{1}\{W(CO)_5\}_2]^{\cdot-}$	215	202	703	200	2.0062
$\mathbf{2}^{\cdot-}$ [8]	259	159	518	/	[c]
$[\mathbf{2}\{Cr(CO)_5\}_2]^{\cdot-}$	186	160	650	40 [g]	2.0043
$[\mathbf{2}\{Mo(CO)_5\}_2]^{\cdot-}$	176	155	633	87	2.0046
$[\mathbf{2}\cdot W(CO)_5]^{\cdot-}$	103 165 228 [d] 256		580 [e]	[c]	2.0057
$[\mathbf{2}\{W(CO)_5\}_2]^{\cdot-}$	160	160	640	150	2.0065
$\mathbf{3}^{\cdot-}$ [8]	248	165	579	/	[c]
$[\mathbf{3}\{Cr(CO)_5\}_2]^{\cdot-}$	170	170	720	[e]	2.0041
$[\mathbf{3}\cdot Mo(CO)_5]^{\cdot-}$	130 150 230 [d] 330		620 [e]	[c]	2.0044
$[\mathbf{3}\{Mo(CO)_5\}_2]^{\cdot-}$	160	160	700	98	2.0045
$[\mathbf{3}\cdot W(CO)_5]^{\cdot-}$	225	112	641	[c]	2.0056
$[\mathbf{3}\{W(CO)_5\}_2]^{\cdot-}$	160	160	700	175	2.0064

[a] Coupling constants a_X in μT (1 μT = 0.01 Gauss). [b] ^{53}Cr: 9.5%, $I = 3/2$; ^{95}Mo: 15.7%, $I = 5/2$; ^{97}Mo: 9.5%, $I = 5/2$; ^{183}W: 14.4%, $I = 1/2$. [c] Not observed or reported. [d] Assignment uncertain. [e] Average for a_N calculated from total spectral width. [f] $a_{^{13}C} = 92$ μT (8 C_{eq}). [g] $a_{^{13}C} = 80$ μT (8 C_{eq} [2]).

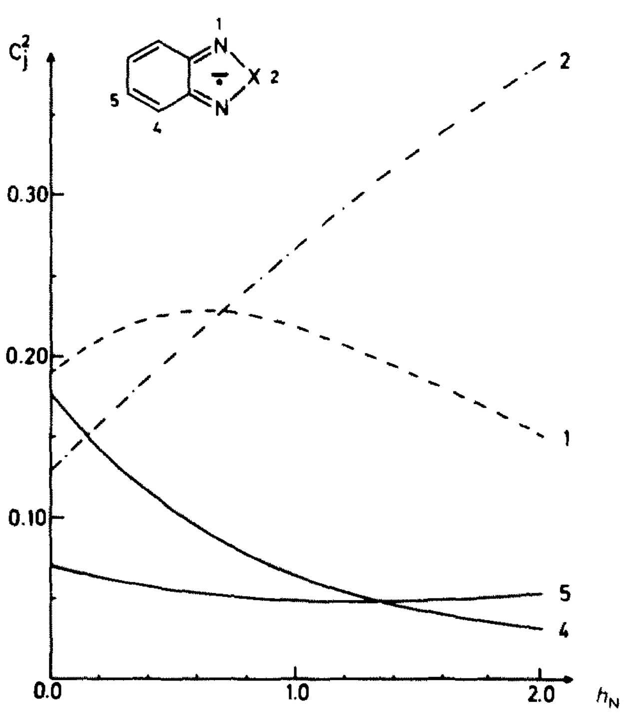


Fig. 5. Hückel MO calculated dependence of the squared π MO coefficients c_j^2 (= π spin populations) on the nitrogen Coulomb integral parameter h_N for the lowest unoccupied·MO (LUMO) of 2,1,3-benzochalcogenadiazoles. Other parameters used: $k_{CN} = 1.$, $k_{NX} = 0.7$, $h_X = 1.1$ [8].

resonances was observed in both instances, no coalescence occurred even at a solvent temperature of 120°C. Taking account of the different time scales of ESR ($\sim 10^{-7}$ s) and ^{1}H NMR ($\sim 10^{-2}$ s) spectroscopy, it becomes evident that the neutral molecules and their radical anions are very different complex ligands, differing not only in their reactivities [3] but also in respect of their coordination pattern.

Experimental

The ligands 2,1,3-benzothiadiazole (**2**) and 2,1,3-benzoselenadiazole (**3**) were obtained from EGA and used without further purification. 2,1,3-Benzoxadiazole (benzofurazan) (**1**) was prepared from benzofuroxan according to a published procedure [17]. Metal hexacarbonyls were obtained from Alfa-Ventron.

The neutral complexes [**2** · W(CO)$_5$] and [**3** · W(CO)$_5$] were prepared by treating a W(CO)$_5$ · THF solution with the ligand in THF. After evaporation of the solvent and removal of remaining W(CO)$_6$ under high vacuum, the complex was recrystallized from acetone. Yields from 1/1 reactions were approximately 60%. Attempts to prepare neutral 1/2 complexes were not successful.

[**2** · W(CO)$_5$]: red crystals; Found: C, 28.73; H, 0.94; N, 5.96. $C_{11}H_4N_2O_5S$ calcd.: C, 28.72; H, 0.88; N, 6.09%. ν(CO) (cm^{-1}, hexane) 2077, 1946, 1925. λ_{max} (cm^{-1}, hexane) 19500, 25000. ^{1}H NMR (270 MHz, C_7D_8, TMS) 300 K: δ 6.71 (1H, dd), 6.83 (1H, dd), 7.25 (1H, d), 7.47 ppm (1H, d); $^3J(4,5) \simeq {}^3J(6,7) = 9.2$ Hz, $^3J(5,6) = 6.4$ Hz. 393 K: δ 6.87, 7.01, 7.38, 7.62 ppm (1H each, all broad).

[**3** · W(CO)$_5$]: purple crystals; Found: C, 26.19; H, 0.97; N, 5.72. $C_{11}H_4N_2O_2Se$ calcd.: C, 26.06; H, 0.80; N, 5.53%. ν(CO) (cm^{-1}, hexane) 2078, 1947, 1927. λ_{max} (cm^{-1}, hexane) 18300, 24200. ^{1}H NMR (270 MHz, C_7D_8, TMS) 300 K: δ 6.51 (1H, dd), 6.64 (1H, dd), 7.14 (1H, d), 7.24 (1H, d); $^3J(4,5) \simeq {}^3J(6,7) = 9.2$ Hz, $^3J(5,6) = 6.5$ Hz. 393 K: 6.58, 6.73, 7.16, 7.28 ppm (1H each, all broad).

The radical solutions were prepared by dissolving ca. 2 mg of the ligand and ~ 10 mg of metal hexacarbonyl in 1 ml THF and by treating this mixture with a freshly generated potassium mirror in a sealed glass system. The reaction was accompanied by CO evolution and yielded radical complexes which were persistent in solution for several weeks. Slow formation of the binuclear species from mononuclear complexes was observed with the combinations of the heavier elements (Fig. 3).

The ESR instrumentation and spectra analysis have been described before [18]. The ^{1}H NMR spectra were recorded with a Bruker WH 270 system, CO infrared frequencies were measured on a Perkin-Elmer 283 B spectrometer. Absorption maxima were determined on a Pye Unicam SP 1800 spectrophotometer. Elementary analyses were carried out in the laboratories of Prof. Ried at the University of Frankfurt.

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