

Contribution from the Chemistry Department,  
J. W. Goethe Universität, D-6000 Frankfurt/Main, West Germany

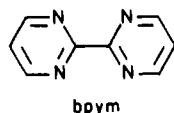
## Mono- and Binuclear Tri- and Tetracarbonyl Complexes of Chromium(0), Molybdenum(0), and Tungsten(0) with the 2,2'-Bipyrimidine Radical Anion

WOLFGANG KAIM

Received September 27, 1983

Mono- and binuclear radical complexes  $[(\text{CO})_x\text{M}]_2\text{bpy}m]^-$  ( $x = 1, 2$ ;  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{bpy}m = 2,2'$ -bipyrimidine) have been studied by high-resolution electron spin resonance (ESR). The unpaired electron was found to reside predominantly in the LUMO of the heterocycle; HMO-McLachlan calculations were used to interpret the hyperfine coupling constants. The bis(molybdenum tetracarbonyl) complex was found to undergo successive replacement of two axial CO groups by  $\text{PBU}_3$  ligands. A  $\pi^*/\sigma^*$  hyperconjugation model has been used to account for the facile CO substitution and for the spin transfer to the peripheral  $^{31}\text{P}$  nuclei. An unexpected behavior was found for the  $g$  values of the complexes, which were generally lower than the  $g$  of the free ligand. This result points to a strong contribution from a low-lying electronically excited state to the radical ground state.

Binuclear transition-metal complexes of 2,2'-bipyrimidine (bpy) have received increasing attention in recent years,<sup>1-6</sup> because bpy can act as a doubly bidentate, bridging ( $\mu$ ) ligand with delocalized  $\pi$  bonding.



2,2'-Bipyrimidine thus combines the chelating properties of ligands such as 2,2'-bipyridine with the bridging function of ligands such as the 1,4-diazines (pyrazines).<sup>7</sup> Especially noteworthy is the fact that bpy can hold together two metal atoms at a distance of approximately 5 Å (assuming a metal-nitrogen bond length of 2 Å); this is very short when compared to metal-metal distances in other molecule-bridged systems.<sup>8</sup> Accordingly, such complexes have been studied in order to investigate ligand-mediated electronic interactions between metal centers,<sup>1-3,5</sup> especially in complexes involving  $\text{Ru}^{\text{II}}$  ( $d^6$ ).<sup>1,2,5</sup>

In 1982, Overton and Connor<sup>4</sup> reported mono- and heterobinuclear  $d^6$  metal carbonyl complexes  $(\text{CO})\text{M}-\text{bpy}m-\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ); reduction experiments on the molybdenum complexes led, however, to little characterized species.<sup>4</sup> In continuation of our studies of radical complexes of group 6 B metal carbonyls with unsaturated N-heterocycles<sup>9</sup> and in view of the fact that bpy itself forms a persistent anion radical,<sup>10</sup> we have undertaken an ESR study of mono- and binuclear radical complexes of bpy with tetracarbonyl fragments of chromium, molybdenum, and tungsten. Since metal carbonyl complexes containing anion radical ligands can undergo facile CO substitution by group 5A ligands,<sup>9e,11</sup> we have also reacted the binuclear molybdenum radical complex with tri-*n*-butylphosphine.

### Experimental Section

**Materials and Radical Generation.** 2,2'-Bipyrimidine and metal hexacarbonyls were purchased from Alfa-Ventron. The radical solutions were most conveniently prepared by dissolving ca. 2 mg of the heterocycle and ca. 10–20 mg of metal hexacarbonyl in 0.5–1 mL of THF and by reacting this mixture with a freshly prepared potassium mirror in a sealed glass sytem under high vacuum. Rapid CO evolution and coloring were usually observed after contact of the solution with potassium until an equilibrium was reached. In the ligand substitution experiment, ca. 50 mg of *P-n-Bu*<sub>3</sub> was added to the solution of the binuclear molybdenum radical complex. Although the overall concentration of the paramagnetic complexes remained low, the radical solutions were persistent for several weeks at room temperature. These radical solutions could also be obtained in a stepwise fashion by both possible reaction sequences: reaction of the preformed bpy anion radical<sup>10</sup> with  $\text{M}(\text{CO})_6$  or treatment of bpy in THF with  $\text{M}(\text{CO})_6/[\text{M}_2(\text{CO})_{10}]^{2-}$  solutions in THF gave identical results.<sup>9d</sup>

**ESR Instrumentation and Spectra Analysis.** ESR spectra were recorded on a Varian E9 instrument.  $g$  values were determined by comparing resolved and overmodulated spectra of the radical complexes and of the perylene radical anion in 1,2-dimethoxyethane ( $g = 2.002656$ )<sup>9</sup> in an ESR double cavity.

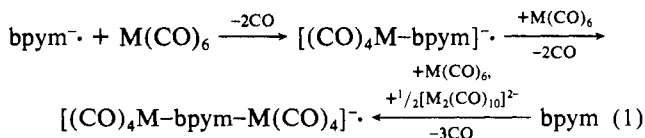
The splitting patterns of the spectra were analyzed by the computer simulation technique (cf. Figure 1) using the program ESPLOT.<sup>9</sup> This program takes into account that isotope combinations can lead to a superposition of spectra, especially for binuclear radical complexes where combinations with  $\text{M}(I=0)-\text{M}(I=0)$ ,  $\text{M}(I \neq 0)-\text{M}(I=0)$ , and  $\text{M}(I \neq 0)-\text{M}(I \neq 0)$  can occur. This phenomenon has been handled by calculating the statistical distribution according to

$$W = p^n(1-p)^{m-n} \binom{m}{n}$$

where  $W$  is the probability of the isotope combination,  $p$  is the relative abundance of the isotope,  $m$  is the total number of equivalent nuclei in one group, and  $n$  is the number of isotopes with the relative abundance  $p$ . Thus, for the binuclear ( $m = 2$ ) tungsten complex with  $p = 0.14$  ( $^{183}\text{W}$ ,  $I = 1/2$ ) the probabilities of isotope combinations are 0.7396 ( $n = 0$ ), 0.2408 ( $n = 1$ ), and 0.0196 ( $n = 2$ ). The magnitudes of the isotope coupling constants are best determined by inspecting the amplified wing sections of the spectra (cf. Figure 2) where the satellite lines belonging to the dominant isotope combinations show up most clearly.

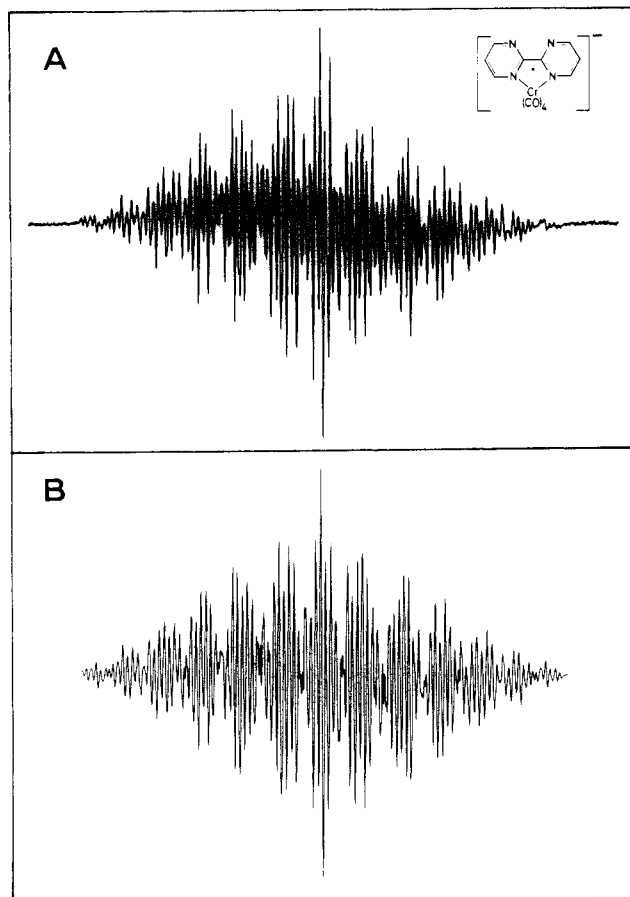
### Results and Discussion

**Formation of Radicals.** The reactions of the bpy radical anion in THF with excess metal hexacarbonyl result in the formation of first mono- and then binuclear tetracarbonyl radical complexes (1). Radical complex formation is also



effected by the reaction of metal hexacarbonyl/deca-

- Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
- Dose, E. V.; Wilson, L. *J. Inorg. Chem.* **1978**, *17*, 2660.
- Petty, R. H.; Welch, B. R.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 611.
- Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53.
- Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, *21*, 3706.
- Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, *2*, 279.
- Cf. Kaim, W. *Angew. Chem.* **1983**, *95*, 201; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 171.
- Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.
- (a) Kaim, W. *Inorg. Chim. Acta* **1981**, *53*, L151. (b) Kaim, W. *Chem. Ber.* **1982**, *115*, 910. (c) Kaim, W.; Kasack, V. *Angew. Chem.* **1982**, *94*, 712; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 700. (d) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504. (e) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171. (f) Kaim, W. *J. Organomet. Chem.* **1984**, *264*, 317. (g) Kaim, W. *Z. Naturforsch., B* **1984**, *39B*, 801.
- Geske, D. H.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 1651.
- Cf.: Creber, K. A. M.; Wan, J. K. S. *Can. J. Chem.* **1983**, *61*, 1017. Weir, D.; Wan, J. K. S. *J. Organomet. Chem.* **1981**, *220*, 323.

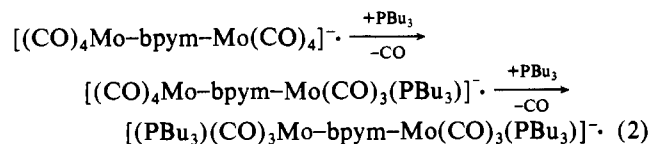


**Figure 1.** (A) ESR spectrum of the tetracarbonyl(2,2'-bipyrimidine)chromium(0) radical anion at 300 K in THF. (B) Computer simulation with the data from Table I and a line width of 11  $\mu\text{T}$  (675 theoretical lines).

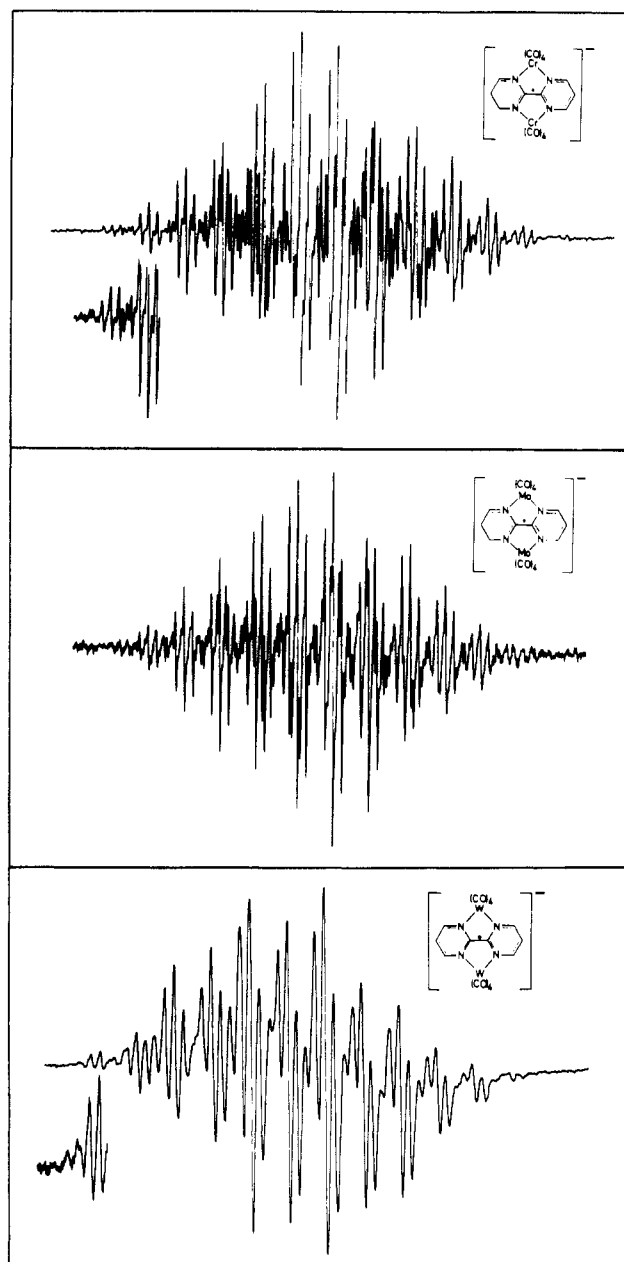
carbonyldimetalate solutions with the neutral ligand; most conveniently, the radical complexes may be generated in three-component reactions of  $\text{M}(\text{CO})_6$ , bpym, and an alkali metal such as K in THF (1).

Successive complexation according to (1) is observed for all three metal carbonyls used. Whereas the formation of binuclear species is fairly rapid in the cases of molybdenum and tungsten,<sup>9b</sup> the mononuclear chromium complex does not undergo further complexation very fast and can, therefore, easily be observed as a separate species (Figure 1).

For the dimolybdenum complex we have also studied the substitution of CO groups by tri-*n*-butylphosphine. This particular set of reactants has been chosen because reference ESR data are available for related molybdenum complexes of the 2,2'-bipyridine radical anion.<sup>15</sup> Phosphorus ligands are very suitable for ESR monitoring of ligand substitution because of the large nuclear magnetic moment of <sup>31</sup>P (100%,  $I = 1/2$ ).<sup>9e</sup> Successive replacement of two CO ligands was observed (2); however, the exchange for the second P-*n*-Bu<sub>3</sub> ligand proved to be rather slow and was accomplished only after some days at room temperature.



**ESR Parameters. Coupling Constants.** The mono- and binuclear radical complexes exhibit well-resolved ESR spectra (Figures 1 and 2) in which hyperfine coupling of the unpaired electron with the nuclei of the heterocycle and with the metal isotopes is evident.



**Figure 2.** ESR spectra of binuclear complexes of the 2,2'-bipyrimidine radical anion with tetracarbonylchromium(0), -molybdenum(0), and -tungsten(0). Amplified low-field wing sections are shown for Cr and W in order to illustrate metal isotope splitting. Anisotropic line broadening<sup>9e</sup> impairs the inversion symmetry of the spectra.

A spectrum of the bis(tetracarbonylmolybdenum) radical complex was published before;<sup>4</sup> however, an analysis of the spectrum was not given.<sup>4</sup> Table I summarizes coupling constants and *g* values of most of the radicals observed; the mononuclear complexes of molybdenum and tungsten tetracarbonyl were always accompanied by the binuclear species and could, therefore, not be analyzed in detail.

The ESR data clearly indicate that the paramagnetic species obtained are ligand-centered radicals, i.e. complexes of  $(\text{CO})_4\text{M}$  ( $d^6$ ) fragments with the 2,2'-bipyrimidine radical anion.<sup>12</sup> For the interpretation of trends in the coupling constants of the  $D_{2h}$  symmetric species, a Hückel-McLachlan molecular orbital correlation for the ligand radical anion was calculated, in which increasing interaction at the nitrogen

(12) Cf. also electrochemical studies on  $\text{Ru}^{\text{II}}\text{bpym}$  complexes: Watanabe, J.; Saji, T.; Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 327. Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

Table I. Coupling Constants  $a_X$  ( $\mu\text{T} = 0.01 \text{ G}$ ) and  $g$  Values of the 2,2'-Bipyrimidine Radical Anion and Its Complexes

radical	$a_{\text{N}(1,3)}$	$a_{\text{H}(5)}$	$a_{\text{M}^c}$	$g$
bpym <sup>-a</sup>	141	15	498	$a$
bpym <sup>-b</sup>	143	15	492	2.0030
[bpymCr(CO) <sub>4</sub> ] <sup>-</sup>	239 (1)	24	500	$d$ 2.0026
	152 (3)	57		
[bpym(Cr(CO) <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	234	52	503	103 2.0022
[bpym(Mo(CO) <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	228	53	495	105 2.0022
[bpym(Mo <sub>2</sub> (CO) <sub>7</sub> (PBu <sub>3</sub> ))] <sup>-</sup>	hfs unresolved except for $a^{31\text{P}e}$			2.0023
[bpym(Mo(CO) <sub>3</sub> (PBu <sub>3</sub> ) <sub>2</sub> )] <sup>-</sup>	220	54	484	$f$ 2.0025
[bpym(W(CO) <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	238	61	475	270 2.0007

<sup>a</sup> Cathodic reduction in DMF; 0.1 M Et<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>; no  $g$  value reported.<sup>10</sup> <sup>b</sup> Reduction with K in THF/0.5 M 18-crown-6. <sup>c</sup> <sup>53</sup>Cr, 9.5% natural abundance,  $I = 3/2$ ; <sup>95,97</sup>Mo, 25.4%,  $I = 5/2$ ; <sup>183</sup>W, 14.3%,  $I = 1/2$ . <sup>d</sup> Not observed. <sup>e</sup>  $a^{31\text{P}} = 1650 \mu\text{T}$  (1 P). <sup>f</sup> Not observed,  $a^{31\text{P}} = 1398 \mu\text{T}$  (2 P).

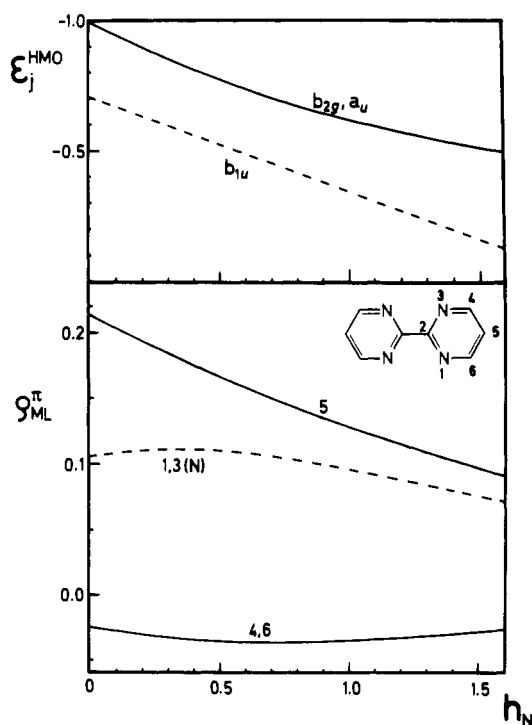


Figure 3. Results from Hückel MO calculations on 2,2'-bipyrimidine, depending on the Coulomb integral parameter  $h_N$ : (top) orbital energies  $\epsilon_j(\beta)$  of the lowest three unoccupied  $\pi$  MOs; (bottom) McLachlan  $\pi$  spin densities  $\rho_{\text{ML}}^\pi$  for the radical anion (orbital  $b_{1u}$  singly occupied) with a McLachlan parameter  $\lambda = 1.2$ .<sup>20</sup>

centers was simulated by an increase of the nitrogen Coulomb integral parameter  $h_N$  (Figure 3).<sup>9d,13</sup>

While the nitrogen hyperfine splitting is known to increase considerably just upon complexation by the group 6B metal carbonyls,<sup>9,14-16</sup> the ring proton coupling constants show only slight variations. The parameter  $a_{\text{H}(5)}$  decreases upon complexation along the series Cr, Mo, and W, in agreement with the behavior of  $\rho_{\text{ML}}^\pi$  with increasing  $h_N$  (Figure 3). The behavior of  $a_{\text{H}(4,6)}$ , on the other hand, is less clear; although the parameter seems to increase in that series, it may actually decrease because the HMO-McLachlan calculations suggest small negative  $\pi$  spin populations at positions 4 and 6.

(13) 2,2'-Bipyridine radical complexes: Kaim, W. *Chem. Ber.* **1981**, *114*, 3789.

(14) Franz, K. D.; tom Dieck, H.; Krynytz, U.; Renk, I. W. *J. Organomet. Chem.* **1974**, *64*, 361.

(15) tom Dieck, H.; Franz, K. D.; Hohmann, F. *Chem. Ber.* **1975**, *108*, 163. Cf. also: Franz, K. D. Thesis, Universität Frankfurt, 1974.

(16) Hunter, J. A.; King, B.; Lindsell, W. E.; Neish, M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 880.

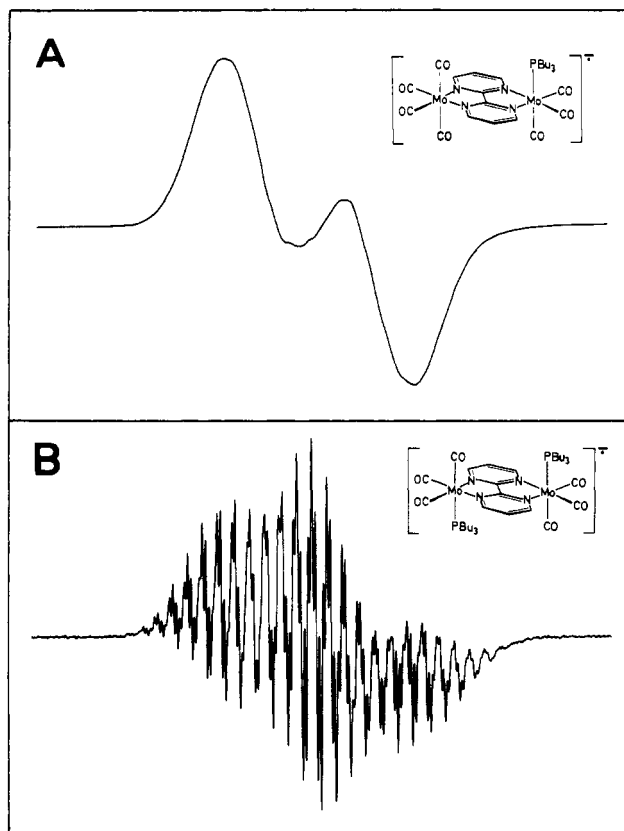


Figure 4. ESR spectra of the monosubstituted (A) and of the disubstituted (B) product from the reaction of the radical anion  $[(\text{CO})_4\text{Mo}]_2\text{bpym}]^-$  with tri-*n*-butylphosphine.

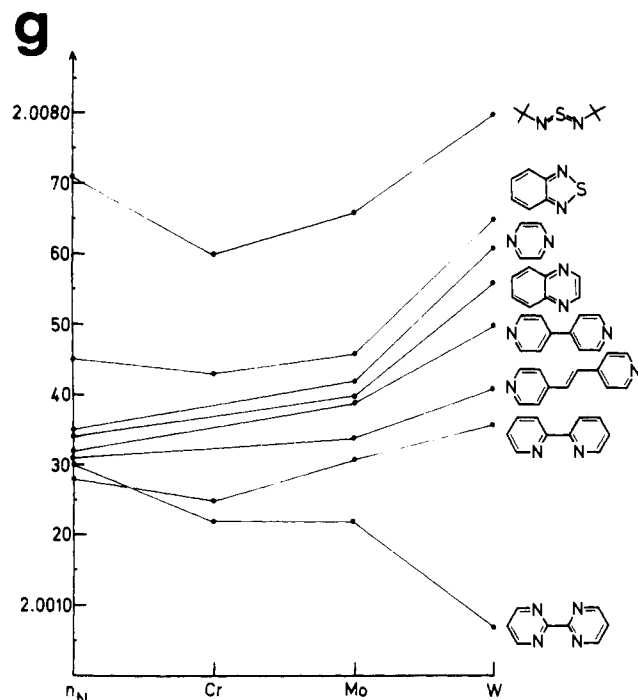
The metal hyperfine coupling constants show the characteristic pattern observed in other chelate radical complexes:<sup>14-16</sup> in contrast to the situations with terminal pentacarbonyl substituents where  $a_{\text{W}} > a_{\text{Mo}} > a_{\text{Cr}}$ ,<sup>9</sup> the sequence here is  $a_{\text{W}} \gg a_{\text{Mo}} \sim a_{\text{Cr}}$ . This different relation obviously reflects the chelate bonding situation for the metal atoms of different radii.<sup>13</sup>

Exchange of CO by PBu<sub>3</sub> can be easily monitored by ESR spectroscopy (Figure 4). Although such substitutions are usually found to proceed fairly rapidly,<sup>11</sup> the second PBu<sub>3</sub> ligand was introduced into the dimolybdenum complex only at a rather slow rate (2). A distinction between the two configurational alternatives, axial or equatorial (cis or trans), should be possible by using the <sup>31</sup>P splittings as a source of information. Equatorial substitution would leave the <sup>31</sup>P nuclei in the nodal plane of the spin-bearing heterocyclic  $\pi$  system, and a hyperfine coupling  $a^{31\text{P}}$  could only result through indirect spin polarization via the metal atom. In the axial configuration, however, the PR<sub>3</sub> groups adopt a position perpendicular to the nodal plane of the heterocyclic  $\pi$  system; then, a  $\pi^*/\sigma_{\text{M-P}}^*$  hyperconjugation mechanism could give rise to an appreciable <sup>31</sup>P splitting.<sup>17</sup>

From a comparison between the ESR data in Table I and those reported by tom Dieck and co-workers<sup>15</sup> for a *cis*-(tri-*n*-butylphosphine)tricarbonyl(2,2'-bipyridine)molybdenum radical anion, it becomes evident that the substitutions (2) have occurred in the axial positions; the ratios  $a_{\text{N}}(\text{bpy})/a_{\text{N}}(\text{bpym}) = 355 \mu\text{T}/220 \mu\text{T} = 1.61$  and  $a_{\text{P}}(\text{bpy})/a_{\text{P}}(\text{bpym}) = 2550 \mu\text{T}/1524 \mu\text{T}$  (average) = 1.67 are comparable. Such a preference for axial substitution has also been observed in related manganese<sup>18</sup> and rhenium complexes.<sup>11</sup> Thus, the PBu<sub>3</sub>

(17) Balch, A. L. *J. Am. Chem. Soc.* **1973**, *95*, 2723.

(18) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1978**, *161*, C63; **1979**, *181*, 355.



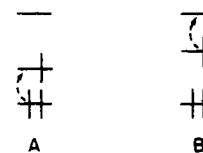
**Figure 5.**  $g$  values of selected radical ligands ( $n_N$ ) and their penta- or tetracarbonylmetalate (group 6B) complexes (data from ref 9, 15, and 16 and Table I).

ligands adopt a position that leads to maximum hyperconjugative interaction and, therefore, to a large  $^{31}\text{P}$  coupling constant. The facile ligand substitution may then be rationalized as a result of less  $\pi$  back-bonding because of the hyperconjugatively transmitted negative charge on the cis carbonyls. Similarly, the photochemical labilization of cis carbonyls in such complexes has been explained by a delocalization of the metal-to-ligand charge-transfer (MLCT) excited state (which involves the ligand radical anion) over the cis carbonyls.<sup>6</sup>

**$g$  Values.** The most surprising result of these ESR studies concerns the  $g$  values of the 2,2'-bipyrimidine radical complexes. In all related instances,<sup>9,14-16</sup> where group 6B metal carbonyls form complexes with nitrogen-containing radical anions, the  $g$  values increase along the series  $g(\text{Cr}) < g(\text{Mo}) \ll g(\text{W})$  (Figure 5).

According to the theory of isotropic  $g$  values (3),<sup>19</sup> the deviations of  $g$  from the value  $g_e = 2.0023$  of the free electron depend on the spin-orbit coupling factors  $\zeta_k$  of the contributing

**Scheme I**



atoms, and this parameter is especially large for the heavy tungsten atom. The reason for  $\Delta g$  is the mixing of excited

$$g = g_e - \frac{2}{3} \sum_i \sum_n \sum_{k,j} \frac{\langle \psi_0 | \zeta_k L_{ik} \delta_k | \psi_n \rangle \langle \psi_n | L_{ij} \delta_j | \psi_0 \rangle}{E_n - E_0} = g_e + \Delta g \quad (3)$$

states with nonzero angular orbital moments to the radical ground state. The direction of that deviation, i.e. the sign of  $\Delta g$ , is determined by the sign of the energy difference  $E_n - E_0$  where  $E_0$  is the energy of the singly occupied molecular orbital and  $E_n$  are the orbital energies of either empty or doubly occupied MOs. Only contributions with  $E_n$  close to  $E_0$  are significant since the difference  $E_n - E_0$  is in the denominator (3).

The case  $g > g_e$  may now be explained by a situation  $E_n < E_0$ ; i.e. the dominating excited states arise from excitations of electrons from doubly occupied orbitals into the singly filled MO (Scheme IA). Apparently, this situation prevails for almost all complexes of group 6B metal carbonyls with N-containing radical anions (Figure 5). In contrast,  $g < g_e$  means that there is a predominant contribution from a nearby excited state that arises from the excitation of the odd electron into an empty molecular orbital, i.e.  $E_n > E_0$  (Scheme IB).

We cannot offer as yet an explanation why this reversed relation occurs only for the 2,2'-bipyrimidine radical complexes; simple HMO energies of the ligand alone do not suggest the presence of a very low-lying excited state of the ligand radical anion (Figure 3). In a recent report, Moore and Petersen<sup>6</sup> have demonstrated via photochemical studies that the metal-to-ligand charge transfer (MLCT) and ligand field (LF) excited states in metal tetracarbonyl complexes of bpym overlap to a large extent; however, this is also true for some related complexes of 2,2'-bipyridine.<sup>6</sup> More elaborate calculations of bpym metal ( $d^6$ ) complexes are needed in order to elucidate the nature of the electronic interactions; in any case, 2,2'-bipyrimidine seems to be a special ligand with peculiar properties.

**Acknowledgment.** Research on electron-transfer reactions in organometallic chemistry is supported by Deutsche Forschungsgemeinschaft (DFG).

**Registry No.** [bpymCr(CO)<sub>4</sub>]<sup>-</sup>, 91742-27-7; [bpym(Cr(CO)<sub>4</sub>)<sub>2</sub>]<sup>-</sup>, 91742-28-8; [bpym(Mo(CO)<sub>4</sub>)<sub>2</sub>]<sup>-</sup>, 82532-99-8; [bpym(Mo<sub>2</sub>(CO)<sub>7</sub>(PBU<sub>3</sub>)]<sup>-</sup>, 91742-29-9; [bpym(Mo(CO)<sub>3</sub>(PBU<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, 91742-30-2; [bpym(W(CO)<sub>4</sub>)<sub>2</sub>]<sup>-</sup>, 91742-31-3; Cr(CO)<sub>6</sub>, 13007-92-6; Mo(CO)<sub>6</sub>, 13939-06-5; W(CO)<sub>6</sub>, 14040-11-0; bpym<sup>-</sup>, 64506-26-9.

(19) Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, p 452.

(20) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.