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Metal π Complexes of Benzene Derivatives. 46.[1] Communication between Chromium(I) and Molybdenum(III) in the Hetera[3]metallocyclophane $\{[(Me_2P\text{-}\eta^6\text{-}C_6H_5)_2Cr](Pr^i\text{-}\eta^5\text{-}C_5H_4)MoCl_2]\}^{\bullet+}$ §

Christoph Elschenbroich,* Thomas Isenburg, and Andreas Behrendt

Fachbereich Chemie, Philipps-Universität,
D-35032 Marburg, Germany

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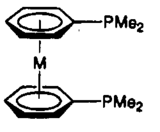
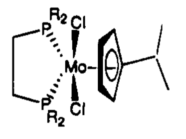
Peripheral substitution at bis(η^6-benzene)metal complexes by R_2P groups affords organometallic diphos-type ligands which may carry an unpaired electron, as in **1**,[2a] or, simultaneously, a unit of charge, as in **2**$^{\bullet+}$.[2b] Given the widespread occurrence of diphos ligands in coordination chemistry, complexes **3** and **4** serving as a recent examples,[4] the special ligands **1** and **2** offer the opportunity to study intramolecular interactions in oligonuclear complexes via electron−electron spin−spin interactions by means of EPR spectroscopy[5] or via redox splittings using cyclic voltammetry.[6] In cases where the structure is known, this study may take the form of unraveling the mechanistic details of the interaction; if for some reason the structure cannot be determined by diffraction methods, valuable structural information may be derived from the zero-field splitting parameters.[7] In this note, we address the question of the extent of interaction between chromium(I) and molybdenum(III), which are parts of a hetera[3]metallocyclophane.[8] This frame provides a well-defined mutual disposition of the two metal atoms.

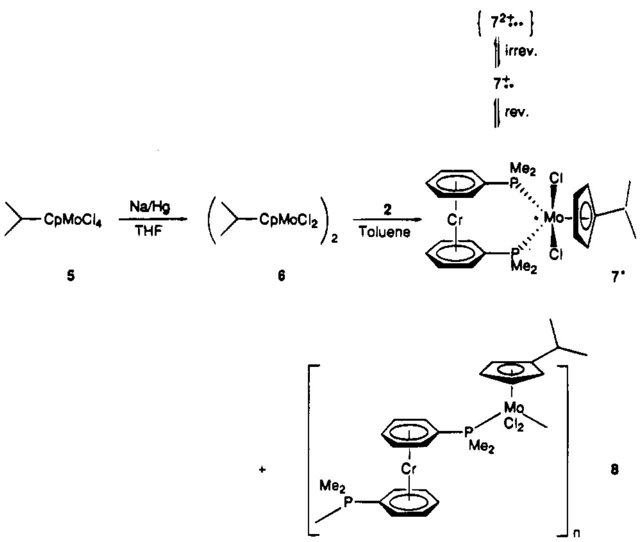


1(M = V)
2(M = Cr)



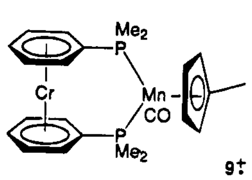
3(R = Ph)
4(R = Me)

Scheme 1



The target molecule **7** was synthesized[3] from (Pr^i-η^5-C_5H_4)$MoCl_4$ (**5**),[9] sodium amalgam, and the organometallic disphosphane **2** following a procedure established by Poli[4] (Scheme 1). The new binuclear complex **7**$^\bullet$ is considerably more stable than **4**, which could only be generated as a transient species.[4b] However, as in the case of the synthesis of **4**, the main product of this reaction is an insoluble material **8** of as yet unknown nature. **7**$^\bullet$ and **8**$^\bullet$ give identical microanalyses. Therefore, **8** possibly represents a polymer in which the diphosphane **2** adopts a bridging rather than a chelating function.

The binuclear chelate **7** contains an 18 valence electron (18 VE) chromium and a 17 VE molybdenum center. Therefore, it exhibits an EPR spectrum which is very similar to those of the mononuclear species **3** and **4**.[4a] In Figure 1, the EPR spectrum of **7**$^\bullet$ in fluid solution is shown with the simulation of the ^{95,97}Mo satellites; in the caption the EPR parameters are given, together with those of **3** for comparison. Since we have shown recently that in the related paramagnetic species $\{[(Me_2P\text{-}\eta^6\text{-}C_6H_5)_2Cr](Me\text{-}\eta^5\text{-}C_5H_4)Mn(CO)\}^{\bullet+}$ (**9**$^{\bullet+}$)hyperfine coupling to *both* central metals is resolved,[10] it was conceivable that for



9$^{+\bullet}$

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§ Dedicated to Professor Henry Taube on the occasion of his 80th birthday.

(1) Part 45: Elschenbroich, Ch.; Bretschneider-Hurley, A.; Hurley, J.; Behrendt, A.; Massa, W.; Wocadlo, S.; Reijerse, E. *Inorg. Chem.* **1995**, *34*, 743.

(2) (a) Elschenbroich, Ch.; Stohler, F. *Chimia* **1974**, *28*, 730. (b) Elschenbroich, Ch.; Heikenfeld, G.; Wünsch, M.; Massa, W.; Baum, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 414.

(3) Procedure for compound **7**$^\bullet$: (Pr^i-η^5-C_5H_4)$MoCl_4$[9] (1.24 g, 3.35 mmol) is suspended in 100 mL of THF and reduced with sodium amalgam (160 mg, 7 mmol, of Na in 10 g of Hg) at room temperature during 5 h to yield an olive green solution of $[(Pr^i\text{-}\eta^5\text{-}C_5H_4)MoCl_2]_2$, which is diamagnetic. This highly air sensitive solution is filtered over a 5 cm layer of silica gel. The solvent THF is removed in vacuo and replaced by 30 mL of toluene. Upon addition of $(Me_2P\text{-}\eta^6\text{-}C_6H_5)_2Cr$ (**2**) (1.17 g, 3.41 mmol), dissolved in 30 mL of toluene, a brown precipitate immediately forms. Stirring is continued for 4 h, and the precipitate (1.56 g) is separated from the brown solution by filtration. This solid material is insoluble in all common solvents. The filtrate is reduced to a volume of 10 mL and layered with 30 mL of *n*-hexane. Upon cooling to −20 °C, 40 mg (0.06 mmol) of **7**$^\bullet$ is obtained as reddish brown microcrystalline material. Anal. Calcd for $C_{24}H_{33}Cl_2CrMoP_2$: C, 47.86; H, 5.52. Found (**7**$^\bullet$): C, 48.31; H, 5.52. Found (insoluble precipitate): C, 47.87; H, 5.79.

(4) (a) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* **1990**, *29*, 2001. (b) Owens, B. E.; Poli, R. *Inorg. Chim. Acta* **1991**, *179*, 229. Green, M. L. H.; Izquierdo, A.; Martin-Polo, J. J.; Mtetwa, V. S. D.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 538.

(5) Atherton, N., *Electron Spin Resonance, Theory and Applications*; Ellis Horwood: Chichester, 1973; Chapter 5. Bencini, A.; Gatteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled Systems*; Springer: Berlin, 1990. Willet, R. D.; Gatteschi, D.; Kahn, O. *Magneto-Structural Correlations in Exchange Coupled Systems*; Reidel: Dordrecht, 1985.

(6) (a) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (b) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *J. Organomet. Chem.* **1995**, *488*, 1.

(7) (a) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* **1970**, *9*, 169. (b) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzee, Y.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1992**, *31*, 3252.

(8) The name *metallocyclophane* designates bis(arene)metal complexes bearing interannular bridges (compare *metallocenophane*: Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702). In *homometallocyclophanes*, the bridges are formed from C units exclusively; in *heterametallocyclophanes* they may also contain other main group or transition elements in their backbone.

(9) The ligand Pr^i-cyclopentadienyl was chosen in order to increase solubility of the educt **5** as well as the product **7**. **5** was prepared as described in ref 4a.

(10) Elschenbroich, Ch.; Isenburg, T.; Metz, B.; Behrendt, A.; Harms, K. *J. Organomet. Chem.* **1994**, *481*, 153.

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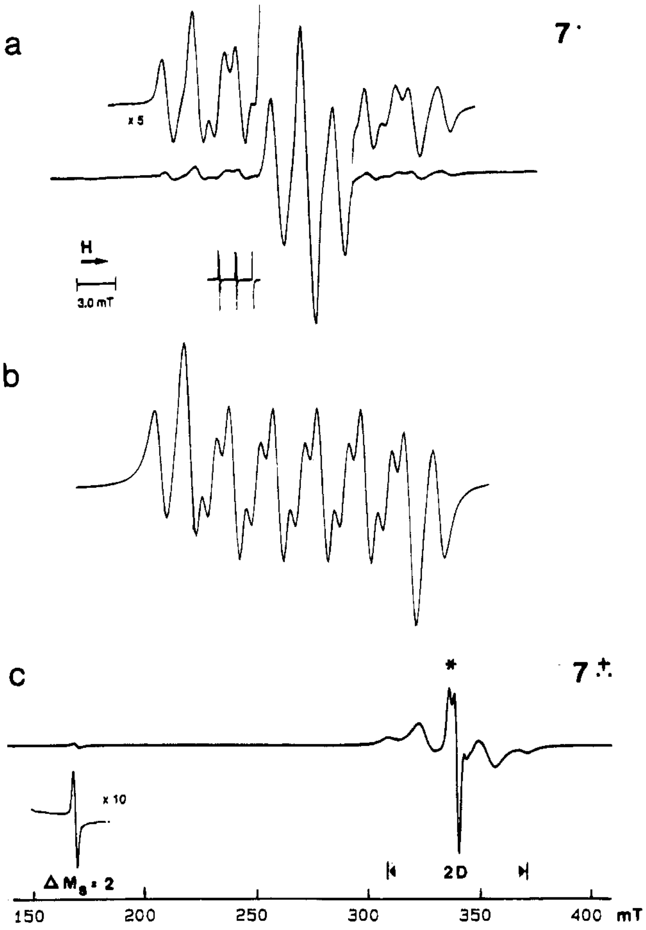

Figure 1. (a) EPR spectrum (X-band) of $7^\bullet$ (toluene, 25 °C, fluid solution), ^{95,97}Mo satellite spectrum shown at higher gain. $\langle g \rangle = 1.982$, $a(^{31}\mathrm{P}) = 2.3$ mT, $a(^{95,97}\mathrm{Mo}) = 3.4$ mT. EPR data for 3:[4a] $\langle g \rangle = 1.986$, $a(^{31}\mathrm{P}) = 2.6$ mT, $a(^{95,97}\mathrm{Mo}) = 2.9$ mT. (b) Simulation of the satellite spectrum. (c) EPR spectrum of $7^{\bullet\bullet+}$ (toluene, −150 °C, rigid solution): $g_1 = 1.977$, $g_{2,3} = 1.981$, $D = 286 \times 10^{-4}$ cm^{-1}, $E < 10 \times 10^{-4}$ cm^{-1}, (*) spectrum of residual $S = {}^1/_2$ species.

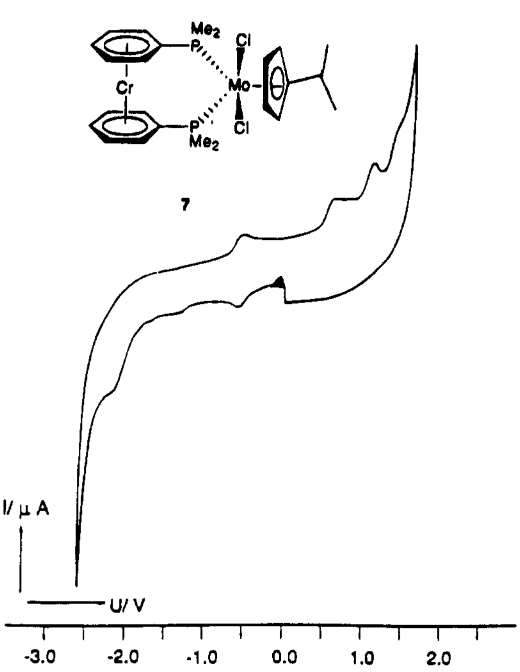

Figure 2. Cyclic voltammetry of $7^\bullet$ in DME/*n*-Bu$_4$NClO$_4$ (0.1 M) at a glassy carbon working electrode, Pt counterlectrode versus SCE. T = 20 °C, scan rate 100 mV s^{-1}. $E_{1/2} = -0.54$ V (ΔE_p = 85 mV, $i_a/i_c \approx 1$, $+7^{+/0}$); E_{pa} 0.63 V (irreversible oxidation of 7^+); $E_{pa} = 1.16$ V (irreversible).

$7^\bullet$ in addition to hyperfine interaction with ^{31}P and ^{95,97}Mo coupling to ^{53}Cr could also be picked up. No indication of this kind is found in the spectrum of $7^\bullet$. Obviously, the s orbital spin population at ^{53}Cr ($I = {}^3/_2$, 9.54%) is too small to generate observable satellites. In the case of $9^{\bullet+}$, the singly occupied orbital is centered at chromium, and a minute amount only is shared by bridging manganese, leading to the coupling constant $a(^{55}\mathrm{Mn}) = 0.8$ G. This exceedingly small interaction owes its detectability to the inherently small linewidths encountered in the EPR spectra of bis(η^6-arene)metal (d^5) species.[11] Conversely, in the neutral radical $7^\bullet$, according to Fenske–Hall MO calculations on the model compound (η^5-C$_5$H$_5$)Mo(PH$_3$)$_2$Cl$_2$,[12] the unpaired electron resides at molybdenum (d^3) in an orbital of 60% Mo 4d$_{z^2}$ content with substantial contribution from phosphorus 3d orbitals. Here a very small hyperfine interaction with the ^{53}Cr nucleus would certainly be hidden under the larger EPR linewidth. Since the ^{95,97}Mo coupling for 7 is somewhat larger than for 3, spin transfer to the bis(η^6-arene)chromium moiety in 7 is apparently negligible.

Since hyperfine coupling failed to provide evidence for intermetallic communication in $7^\bullet$, we turned to electron–electron spin–spin interaction as a probe. A look at the redox potentials $E_{1/2}$ for the constituting moieties reveals that selective one-electron oxidation at chromium to yield the biradical cation $7^{\bullet\bullet+}$ should be feasible since $E_{1/2}(2^{+/0}) = -0.57$ V[2b] and $E_{1/2}(3^{+/0}) = -0.12$ V.[4a] In fact, oxidation of 7 by 4-pyridinecarbaldehyde and immediate cooling to −150 °C lead to an EPR spectrum in rigid solution which undoubtedly is that of a biradical (Figure 1). This conclusion is based on the presence of a half-field ($\Delta M_s = 2$) signal and a typical triplet EPR fine structure in the $g \approx 2$ region which is superimposed on the signal of a residual $S = {}^1/_2$ species. While in the triplet EPR spectrum the zero-field splitting parameter E is too small to be resolved, for D a value of 286×10^{-4} cm^{-1} is obtained. Under the assumption that the point-dipole approximation is valid, by means of the relation $r = (3g\beta/2D)^{1/3}$,[13] an interspin distance of 450 pm is derived. This result agrees very well with the intermetallic distance $r(\mathrm{Cr\cdots Mo}) \approx 460$ pm estimated from molecular models and the consideration of analogous molecules like 9 which yielded to X-ray crystallography.[14] The match between interspin distance from EPR and intermetallic distance is in line with the single occupancy of two metal centered d$_{z^2}$ orbitals which are perpendicularly disposed, each orbital being collinear with the respective π-perimeter–metal axis. In such a geometrical situation and at this intermetal distance, overlap between the two singly occupied metal orbitals (torus of Cr d$_{z^2}$, lobe of Mo 4d$_{z^2}$) should be negligible; i.e., metal–metal bonding is absent. Furthermore, since the g values of the monomolecular component radicals $2^{\bullet+}$ and $4^\bullet$ are close to the free spin value, contributions of spin–orbit coupling to zero-field splitting should be unimportant and electron–electron spin–spin interaction in the biradical cation $7^{\bullet\bullet+}$ can be regarded as purely dipolar.[15]

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[11] Prins, R.; Reinders, F. J. *Chem. Phys. Lett.* **1969**, *3*, 45. Elschenbroich, Ch.; Möckel, R.; Zenneck, U.; Clack, D. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 1008.

[12] Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

[13] Eaton, S. S.; More, K. M.; Savant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

[14] For 7, crystals suitable for an X-ray structure determination could not be obtained.

It has been demonstrated by cyclic voltammetry that mononuclear $\mathbf{3}^{\bullet}$ may be oxidized reversibly to the 16 VE species $\mathbf{3}^{\bullet\bullet+}$,[4a] the latter cation also being accessible as the salt [**3**](BF_4).[16] Since $\mathbf{3}^{\bullet\bullet+}$ constitutes a spin triplet,[12] it was of interest to generate the dinuclear dication $\mathbf{7}^{2+}$ in order to possibly investigate intramolecular interaction between a Cr($S = {}^1/_2$) and a Mo($S = 1$) center. However, as the cyclovoltammetric trace (Figure 2) shows, the redox couple $\mathbf{7}^{2+/+}$ is irreversible. This also applies to CV in the limited scan range $-1.0\ \mathrm{V} < E < +1.2\ \mathrm{V}$. Thus, whereas primary oxidation of $\mathbf{7}^{\bullet}$ at the bis(arene)chromium moiety is reversible, displaying only a small anodic shift of +30 mV relative to mononuclear **2**, secondary oxidation to yield the hypothetical dication $\mathbf{7}^{2+}$ probably leads to metal expulsion, caused by the close vicinity of two cations in the dinuclear complex and assisted by nucleophilic attack of the solvent.

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(15) Complementary studies of $\mathbf{7}^{\bullet\bullet+}$ based on measurements of magnetic susceptibility are unpractical since $\mathbf{7}^{\bullet\bullet+}$ could only be generated in solution, all attempts to isolate analytically pure salts like [**7**](BF_4) being abortive.

(16) (a) Stärker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006. (b) The related salt $[Cp^*MoCl_2(PMe_2Ph)_2]AlCl_4$ has very recently been characterized by X-ray diffraction: Abugideiri, F.; Keogh, D. W.; Kraatz, H.-B.; Pearson, W.; Poli, R. *J. Organomet. Chem.* **1995**, *488*, 29.

Additions and Corrections

1995, Volume 34

Jiann T. Lin,* Shih-Sheng Sun, Jiann Jung Wu, Liangshiu Lee, Kuan-Jiuh Lin, and Yi Fong Huang: Dinuclear Metal Carbonyls Bridged by Pyridyl Ligands Incorporating an Alkyne Entity.

Page 2329. In Figure 2, the *y*-axis values should be multiplied by 10 to read 25 000, 24 000, etc.... In Table 5, footnote *e*, substitute (η^1-**DPB**) for (η^1-**BPB**).

Page 2330. For Figure 3, the caption should read "Electronic spectra of...".

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