BINUCLEAR RADICAL COMPLEXES OF MOLYBDENUM AND TUNGSTEN TETRACARBONYLS WITH BRIDGING N-HETEROCYCLES AND GROUP VA LIGANDS. ESR EVIDENCE FOR A *cis* CONFIGURATION
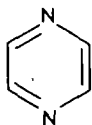
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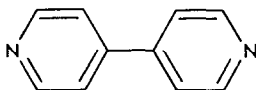
Summary

The reactions of $Mo(CO)_6$ or $W(CO)_6$ and of bridging N-heterocyclic ligands L such as pyrazine or 4,4'-bipyridine with potassium have been studied by ESR spectroscopy in the presence of excess phosphane, phosphite or arsane ligands. In many cases, double substitution at the metals could be observed, yielding binuclear paramagnetic complexes $[(XR_3)(CO)_4M\text{--}L\text{--}M(CO)_4(XR_3)]^{\overline{\cdot}}$ (X = P, As; R = alkyl, aryl, alkoxy; M = Mo, W). ESR investigation of the complexes in THF solution reveals extensive coupling of the unpaired electron with the nuclei ^1H, $^{13}C(CO)$, ^{14}N, ^{31}P, ^{75}As, $^{95,97}Mo$ and ^{183}W. Evidence for a *cis* configuration at the metals is presented, and a π^*/σ^*_{MX} hyperconjugation model is used to account for the facile substitution of CO and for the spin transfer to the peripheral nuclei.

We recently reported the formation of persistent binuclear radical complexes $[(CO)_5M\text{--}L\text{--}M(CO)_5]^{\overline{\cdot}}$ from the reactions of bridging (μ-) N-heterocyclic ligands L and metal hexacarbonyls $M(CO)_6$ with potassium [1,2]. The ease of this electron transfer-assisted ligand substitution at room temperature led us to study the possibility of further exchange of CO at the metal centres by suitable ligands. Trialkyl-phosphanes, -phosphites and -arsanes are such ligands, since they do not easily react with potassium alone and so may be added to the reaction mixture without causing unwanted side reactions. As an additional bonus, the isotopes ^{31}P and ^{75}As have favourable nuclear properties (Table 1) and can be expected to show coupling to the unpaired electron in the complex.

(pz)   (bp)

TABLE 1

PROPERTIES OF THE NUCLEI COUPLING WITH THE UNPAIRED ELECTRON IN THE RADICAL COMPLEXES DESCRIBED: NATURAL ABUNDANCE p. NUCLEAR SPIN I. AND CALCULATED ISOTROPIC HYPERFINE COUPLING CONSTANTS A_{iso} [3]

	Isotope							
	^1H	^{13}C	^{14}N	^{31}P	^{75}As	^{95}Mo	^{97}Mo	^{183}W
p (%)	99.98	1.11	99.64	100	100	15.72	9.46	14.40
I	1/2	1/2	1	1/2	3/2	5/2	5/2	1/2
A_{iso} (mT)	50.8	111.9	55.7	367.6	343.1	−46.2	−47.1	53.6

Presented here are electron spin resonance (ESR) results for the radicals formed in the reactions of pyrazine (pz) or 4,4′-bipyridine (bp) with $Mo(CO)_6$ or $W(CO)_6$ and K in THF, using the following Group VA ligands as co-substrates: PPh_3, P-n-Bu_3, P-i-Pr_3, n-$Bu_2PCH_2CH_2$P-n-Bu_2. $P(OMe)_3$, P(O-i-Pr)$_3$. $AsPh_3$, $AsEt_3$.

Results

Reactivity. Reactions of solutions containing $M(CO)_6$, the heterocycle and an excess of one of the phosphorus ligands with potassium in THF are generally accompanied by CO evolution. In the sealed glass systems used, this CO evolution ceases when an equilibrium is attained [4], and the formation of binuclear bis(tetracarbonyl) complexes (eq. 1) is observed by ESR. The complexes may also be

$$L + 2\,M(CO)_6 + 2\,PR_3 + K \xrightarrow{-4\,CO} \left[(PR_3)(CO)_4M\text{-}L\text{-}M(CO)_4(PR_3)\right]^{\cdot}\,K^+ \qquad (1)$$

generated in a stepwise fashion (cf. eq. 2) by treating bis(pentacarbonylmetal) radical complexes [1] with phosphorus ligands; exchange at the substitution labile metal centres is fairly rapid [5a].

When the bidentate bisphosphane n-$Bu_2PCH_2CH_2$P-n-Bu_2 was used with pyrazine and $W(CO)_6$ in order to achieve further substitution, a radical with ESR parameters virtually identical to those of the complex with P-n-Bu_3 was observed. This result indicates monosubstitution: evidently both phosphorus atoms of the chelate diphosphane could not be induced to coordinate to the same tungsten center [5b,c]. Aryl phosphanes do not undergo clean reactions because they can themselves be reduced to yield P-aryl cleavage products [6].

Arsanes are much less readily introduced in place of CO than are the phosphorus ligands [5]. Using pyrazine and $W(CO)_6$, only the parent radical complex

(2)

$[(CO)_5W-pz-W(CO)_5]^{\div}$ is observed [1a] if an excess of $AsPh_3$ is added. Triethylarsane $AsEt_3$ replaces two CO groups in the paramagnetic complex, albeit very slowly; even after several days at room temperature, both the $AsEt_3$-substituted and unsubstituted species can be detected simultaneously (eq. 2).

ESR parameters. The paramagnetic solutions obtained by the above methods exhibit well resolved ESR spectra, in which extensive hyperfine coupling of the
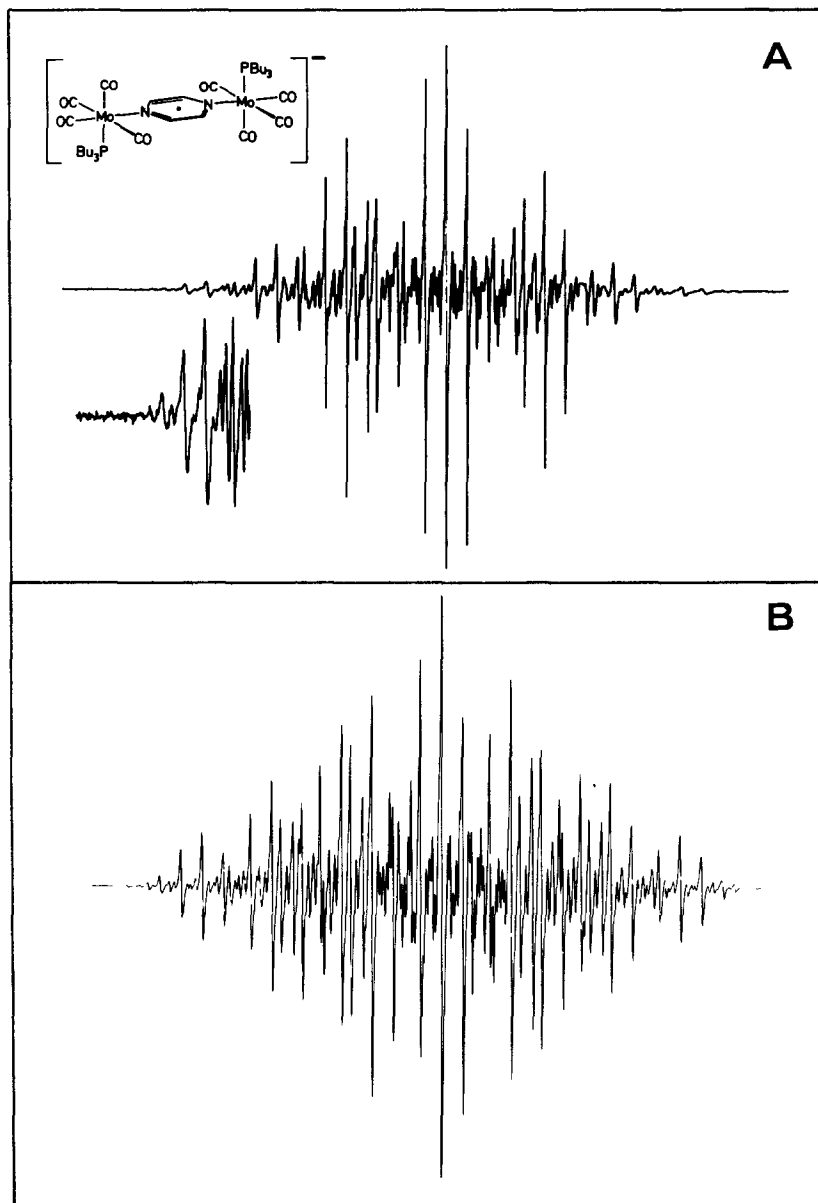

Fig. 1. (A) ESR spectrum of the radical complex $[pz\{Mo(CO)_4(P-n-Bu_3)\}_2]^{\div}$ K^+ at 295 K in THF with amplified low field wing section. (B) Computer assisted spectrum synthesis using the data from Table 2 and a line width of 19 μT.

unpaired electron with various nuclei (Table 1) is evident (Figs. 1–3). Computer-assisted syntheses of the recorded spectra reveal strong broadening of the outer line groups, an effect which is due to the insufficient averaging of anisotropic contributions from coupling constants and g-values. The relatively slow movement of the radical complexes in solution may be partly attributed to the increase in viscosity as an excess of the Group VA ligand was added to the solution, but another cause lies
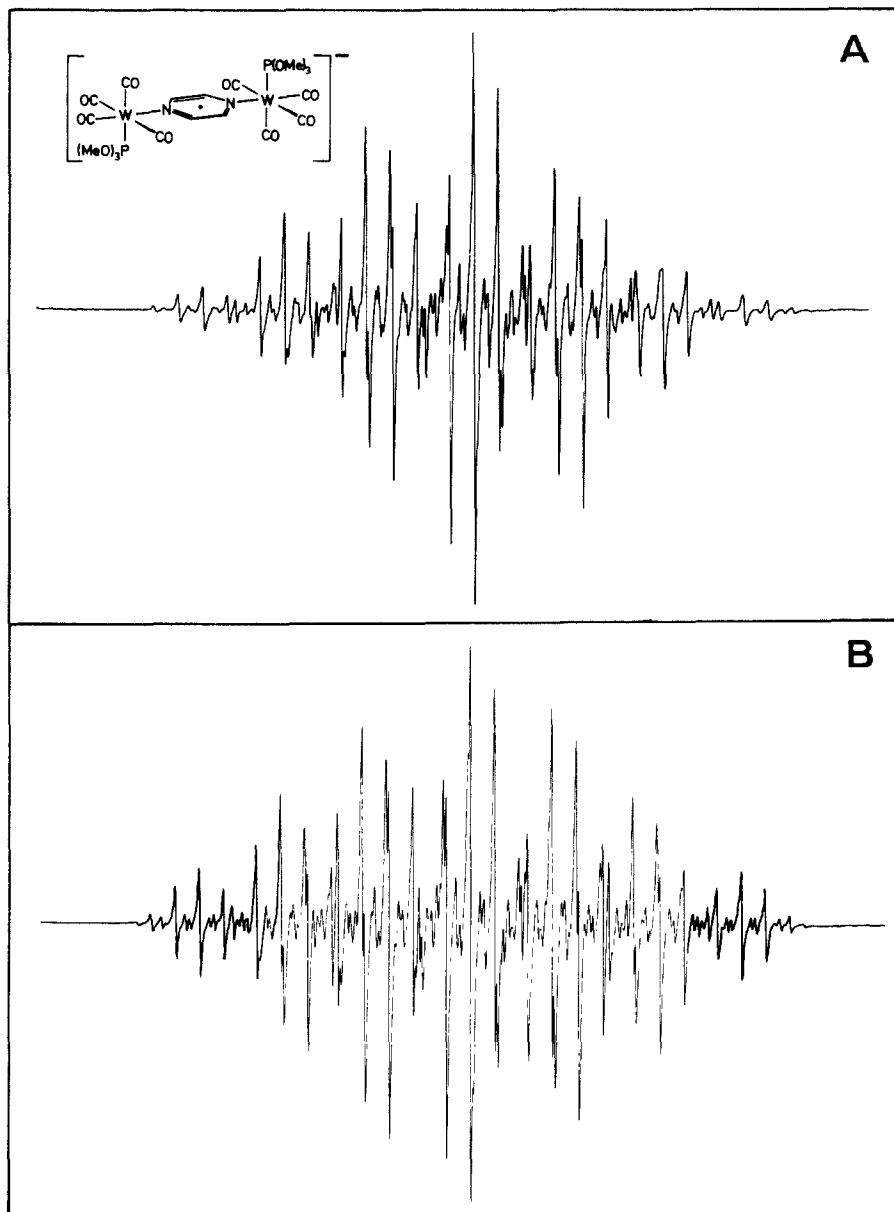
Fig. 2. (A) ESR spectrum of the radical complex $[pz\{W(CO)_4(P(OMe)_3)\}_2]^{\cdot}$ K$^+$ at 300 K in THF. (B) Computer simulation with the data from Table 2, line width 22 μT.
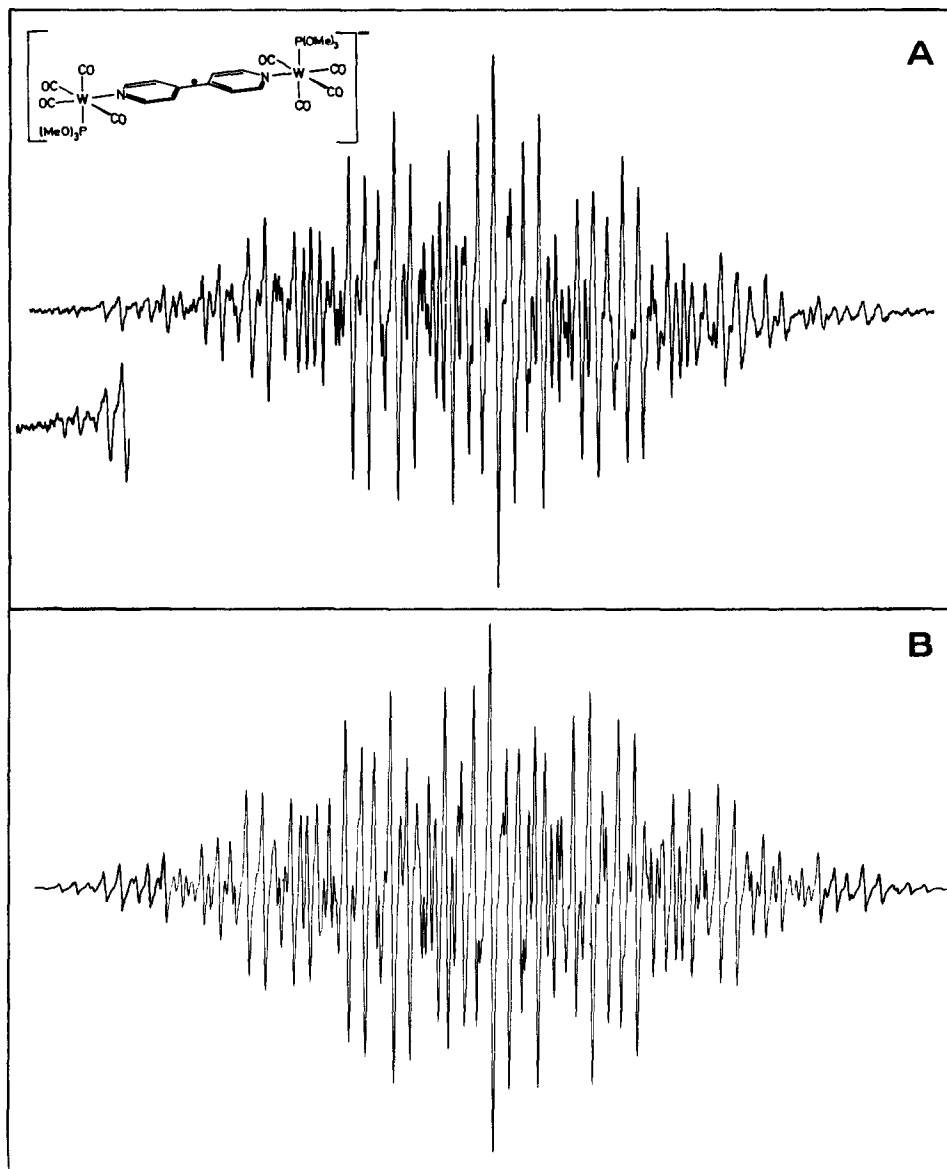
Fig. 3. (A) ESR spectrum of the radical complex [bp{W(CO)$_4$P(OMe)$_3$)}$_2$]$^-$ K$^+$ at 300 K in THF with amplified wing section of that spectrum. (B) Computer simulation using the data from Table 2 and a line width of 13 μT.

in the large moments of inertia of such molecules with a dumbbell-kind of mass distribution [7] (cf. (4)). Nevertheless, all the relevant coupling constants could be determined for the complexes investigated; Table 2 displays the following trends: Whereas the nitrogen and metal coupling constants exhibit very little variation on replacement of the fifth CO substituent by a Group VA ligand, the ring proton couplings and the g values are slightly diminished, thereby indicating that more spin density is withdrawn from the heterocyclic π system towards the coordinated metal

TABLE 2

ESR PARAMETERS OF RADICAL COMPLEXES, COUPLING CONSTANTS a_X IN μT ($1 \mu T = 0.01$ G)

Radical complex	a_{1_H}	a_{14_N}	a_M [c]	a_{31_P}	g
[pz{Mo(CO)$_5$}$_2$]·	253	818	150	/[e]	2.0042
[pz{Mo(CO)$_4$(P-n-Bu$_3$)}$_2$]$^{\bar{}}$	247	808	152	1150[f]	2.0040
[pz{Mo(CO)$_4$(P(O-i-Pr)$_3$)}$_2$]$^{\bar{}}$	246	811	145	977	2.0040
[pz{W(CO)$_5$}$_2$]$^{\bar{}}$	254	823	286	/[e]	2.0061
[pz{W(CO)$_4$(PPh$_3$)}$_2$]$^{\bar{}}$	250	811	286	500	2.0057
[pz{W(CO)$_4$(P-i-Pr$_3$)}$_2$]$^{\bar{}}$	243	810	294	1228	2 0057
[pz{W(CO)$_4$(P-n-Bu$_3$)}$_2$]$^{\bar{}}$	243	815	295	1307	2.0057
[pz{W(CO)$_4$(L)}$_2$]$^{\bar{}}$ [a]	245	814	284	1315	2.0057
[pz{W(CO)$_4$(P(OMe)$_3$)}$_2$]$^{\bar{}}$	240	808	283	1075	2.0058
[pz{W(CO)$_4$(P(O-i-Pr)$_3$)}$_2$]·	245	805	272	1120	2 0058
[pz{W(CO)$_4$(AsEt$_3$)}$_2$]$^{\bar{}}$	250	810	[d]	1530[g]	2.0059
[bp{W(CO)$_5$}$_2$]$^{\bar{}}$	80 (2)	433	163	/[e]	2 0050
	192 (3)[b]				
[bp{W(CO)$_4$(P(OMe)$_3$)}$_2$]$^{\bar{}}$	72 (2)	442	[d]	570	2.0047
	199 (3)[b]				

[a] L = monodentate coordinated n-Bu$_2$PCH$_2$CH$_2$P-n-Bu$_2$. [b] Assignments to positions given in brackets. [c] ^{95,97}Mo or ^{183}W (cf. Table 1). [d] Not observed. [e] Cf. ref. 1 for ^{13}C coupling constants. [f] a_{13_C} (CO, 6C) = 90 μT. [g] $a_{75_{As}}$.

fragments [5]. The redistribution of spin population in the μ-4,4'-bipyridine radical complex is also in agreement with this concept [8]. As expected, the magnitude of the ^{31}P splitting depends critically on the substituents at the phosphorus atom [6,7,9]; electronic and steric effects may play a role [10]. As a rule, the ^{31}P hyperfine splitting is larger in the phosphane than in the corresponding phosphite complexes. Furthermore, for tungsten complexes this parameter is approximately 10% larger than for the corresponding molybdenum species, this may be attributed to the lower lying σ^*_{W-P} orbitals, which are slightly more suitable than the σ^*_{Mo-P} orbitals for interaction with the singly occupied MO of the heterocyclic π system.

Configuration at the metal. An interesting question to be answered by ESR analysis is that of the configuration, *cis* or *trans*, at the metal centres. Only one of the two isomers, *cis/cis* or *trans/trans*, is observed by ESR, symmetry ruling out the mixed species. Assignments made for related tri- or tetra-carbonyl radical complexes of Group VIB [11] and Group VIIB [5,12–14] metals were divided between a *cis* and a *trans* substitution pattern; Alberti and Camaggi [12] have observed a *trans* → *cis* rearrangement in trialkylphosphite/semidione complexes of manganese dicarbonyl, and recently Creber and Wan corrected an earlier *trans* assignment [5b] for related rhenium complexes on the basis of IR studies [5a].

A distinction between the two configurational alternatives should be possible by using the ^{31}P splittings as a source of information. For a *trans/trans* combination, the ^{31}P nuclei would lie in the plane of the spin-bearing heterocyclic π system, and a hyperfine coupling $a(^{31}$P) could only result from indirect spin polarization via the metal atom. For the *cis/cis* configuration, however, the bulky PR$_3$ groups would be expected to adopt preferentially a position perpendicular to the plane of the heterocycle; in this case, a π^*/σ^*_{M-P} hyperconjugation mechanism could give rise to

an appreciable ^{31}P splitting. Previous observations by Alberti and Camaggi [12] lend direct support to this conception.

In order to obtain a quantitative assessment of the configuration of the complex it is necessary to have a reference compound of undisputable geometry and to make use of the modified Heller–McConnell equation 3, where B is a constant, θ is the torsion angle between the heterocyclic π system and the σ_{M-P} bond, and ρ_N is the π spin population at the nitrogen atom. The Heller–McConnell equation was originally

$$a_{31_P} = B \cdot \cos^2\theta \cdot \rho_N \qquad (3)$$

derived to interpret β hydrogen splittings of hydrocarbon radicals [15], but recently, it has also been applied to heteroatomic systems [16,17].

The parameter B for the Mo/P-n-Bu$_3$ combination may be determined from the data for a cis-2,2'-bipyridine complex reported by tom Dieck and coworkers [18]. Taking the Hückel coefficient $c_N^2 = 0.139$ from HMO calculations with $h_N = 0.89$ [19], one has to apply $\rho_N = (2 \cdot c_N)^2 = 4 \cdot c_N^2$ [20] to obtain $B = 4500\ \mu T$. Using this parameter for the complex $[(P\text{-}n\text{-}Bu_3)(CO)_4Mo\text{-}pz\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)]^{\bar{\cdot}}$, for which $\rho_N = c_N^2 = 0.260$ [19] and $a_{31_P} = 1150\ \mu T$ (Table 2), an angle θ of 7.5°, i.e. an almost perpendicular arrangement between the pyrazine π plane and the σ_{Mo-P} bond is calculated:
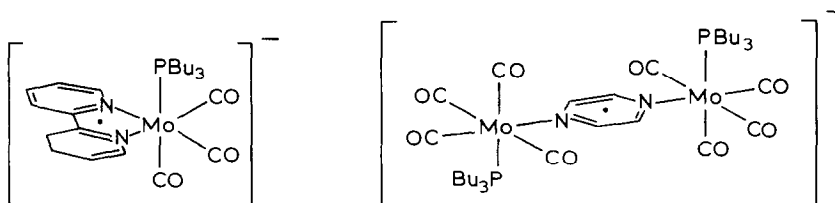
Thus, the PR$_3$ ligand adopts a position which is reasonable from the steric point of view and which leads to maximum hyperconjugative interaction and, thus to a large ^{31}P coupling constant. Future work will focus on the question of the extent to which this hyperconjugative interaction might contribute to the energetic stabilization of this particular radical configuration. It may be added that the photochemical labilization of cis carbonyls in related α diimine complexes has been explained in terms of delocalization of the metal-to-ligand charge transfer excited state (which involves the ligand radical anion) over the cis carbonyls [21]. Since pure π back bonding effects were ruled out as a cause [21], π^*/σ^*_{CO} hyperconjugation may be invoked to account for the spectroscopic and photochemical observations [21,22], viz., weakening of the cis metal/CO bonds as a result of less π back bonding because of hyperconjugatively transmitted negative charge.

Experimental

ESR instrumentation and spectra analysis have been described before [8].

Phosphanes, phosphites and arsanes were purchased from Strem Chemicals and were used without further purification. The radical solutions were prepared by dissolving ca. 2 mg of the heterocyclic ligand, 10 mg of metal hexacarbonyl and approx. 50 mg of the Group VA ligand in THF (0.5–1 ml), and by treating this

mixture with a freshly prepared potassium mirror in a sealed glass system. Rapid CO evolution and development of colour were usually observed after contact of the solution with K, until an equilibrium was reached. Although the overall concentration of the radical complexes was relatively low, the radical solutions were persistent for several weeks at room temperature. The mixed-ligand radical complexes can also be obtained by a two-step substitution reaction; treatment of THF solutions of $[(CO)_5M-L-M(CO)_5]^{\overline{\cdot}}$ with phosphorus ligands results in the rapid formation of the bis(tetracarbonyl) complexes described above.

Acknowledgement

References

1 W. Kaim, (a) Inorg. Chim. Acta, 53 (1981) L151; (b) Chem. Ber., 115 (1982) 910

2 W. Kaim and V. Kasack. Angew. Chem., 94 (1982) 712; Angew. Chem. Int. Ed. Engl., 21 (1982) 700.

3 Data from B.A. Goodman and J.B. Raynor, Adv. Inorg. Radiochem.,13 (1970) 136.

4 W. Kaim, Inorg. Chem., in press.

5 Cf. studies on rhenium semiquinone complexes: (a) K.A.M. Creber and J.K.S. Wan, Can. J. Chem., 61 (1983) 1017; (b) K.A.M. Creber and J.K.S. Wan, Chem. Phys. Lett., 81 (1981) 453; (c) K A.M. Creber, T.I. Ho, M.C. Depew, D. Weir and J.K.S. Wan, Can. J. Chem. 60 (1982) 1504.

6 Cf. W. Kaim, P. Hanel and H. Bock. Z. Naturforsch. B, 37 (1982) 1382.

7 Similar effects were observed e.g. for selenium-containing radical ions: W. Kaim, Z. Naturforsch. B., 36 (1981) 150.

8 W. Kaim, J. Organomet. Chem., 241 (1983) 157.

9 W. Kaim, H. Bock and H. Nöth, Chem. Ber., 111 (1978) 3276; W. Kaim and H. Bock, Chem. Ber., 114 (1981) 1576; W. Kaim, P. Hänel, U. Lechner-Knoblauch and H. Bock, Chem. Ber., 115 (1982) 1265, and J. Org. Chem., in press.

10 C.A. Tolman, Chem. Rev., 77 (1977) 313.

11 D. Weir and J.K.S. Wan, J. Organomet. Chem., 220 (1981) 323.

12 A. Alberti and C.M. Camaggi, J. Organomet. Chem., 161 (1978) C63 and 181 (1979) 355.

13 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Chem. Soc. Dalton, (1977) 551.

14 A.L. Balch, J. Am. Chem. Soc., 95 (1973) 2723; L.S. Benner and A.L. Balch, J. Organomet. Chem., 134 (1977) 121.

15 C. Heller and H. McConnell, J. Chem. Phys., 32 (1960) 1535.

16 H. Bock and W. Kaim, Acc. Chem. Res., 15 (1982) 9.

17 W. Kaim, J. Am. Chem. Soc., in press.

18 H. tom Dieck, K.D. Franz and F. Hohmann, Chem. Ber., 108 (1975) 163.

19 F. Gerson, High Resolution ESR Spectroscopy, Verlag Chemie, Weinheim 1970.

20 D.H. Whiffen, Mol. Phys., 6 (1963) 223.

21 R.W. Balk, T. Snoeck, D.J. Stufkens and A. Oskam, Inorg. Chem., 19 (1980) 3015.

22 Resonance Raman studies: H Daamen, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 39 (1980) 75.