

UV-vis, IR and EPR spectroelectrochemical study of the EC redox transition $[(PR_3)_n(CO)_3(R'-pz)M]^{+/0}$; M = Mo, W; R'-pz = N-alkylpyrazinium; R = isopropyl, cyclohexyl; n = 1 or 2

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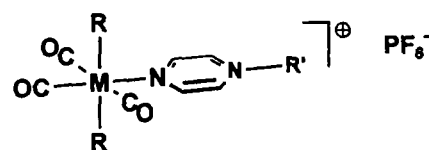
Abstract

The title complexes, isolated as *trans,mer*-configured salts $[(PR_3)_2(CO)_3(R'-pz)M](PF_6)$, display a strong π interaction between the zerovalent metal center and the excellent π acceptor ligands R-pz⁺. The solvatochromism of the long-wavelength metal-to-ligand charge transfer (MLCT) absorption as analyzed in particular for $[(PCy_3)_2(CO)_3(CH_3(CH_2)_{17}-pz)W](PF_6)$ correlates not with established MLCT parameters but with the donor numbers of the solvents. The seemingly reversible one-electron oxidation and reduction processes were studied by spectroelectrochemical techniques with regard to EPR, carbonyl vibrational and UV-vis/NIR spectroscopic features. Whereas oxidation leads to labile M(I) species with 17 valence electrons, the reduction is centered at the R'-pz⁺ ligand and causes a rapid reversible dissociation of one PR₃ group from the metal (EC_{rev} process). Both EPR and IR data suggest pentacoordination at the 16 + δ valence electron centers in the neutral species $[(PR_3)_2(CO)_3(R'-pz)M]^{\cdot}$.

Keywords: Electrochemistry; Molybdenum compounds; Radical ligands; Spectroscopy; Tungsten compounds; Spectroelectrochemistry

1. Introduction

The 16 valence electron fragments $(PR_3)_2(CO)_3M$, M = Mo or W, R = isopropyl (ⁱPr) or cyclohexyl (Cy) have received wide attention because of their ability to form persistent complexes with side-on coordinated molecular H₂ [1,2]. Recent work showed that the back-donating and π bond-forming capacity of these fragments can also be employed to stabilize organometallic mixed-valent ions reminiscent of the Creutz-Taube ion [3,4]. Stable coordination compounds of $(PR_3)_2(CO)_3W$ could also be obtained [5] with *N*-methylpyrazinium cation (mpz⁺) which is a poor σ donor but an excellent π acceptor ligand [5–9]. Accordingly, the crystal structure analysis of *trans,mer*- $[(PCy_3)_2(CO)_3(mpz)W](PF_6)$ revealed an unusually short W⁰-N “single” bond at a distance of 2.101 Å [5].



M = Mo, W

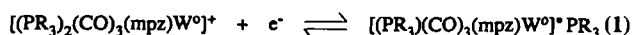
R = -PⁱPr₃, -PCy₃

R' = -CH₃, -(CH₂)₁₇CH₃

As an unsaturated cationic ligand, mpz⁺ is not only a weak σ donor and strong π acceptor, it can also be reduced to a persistent neutral radical species mpz[·] which has been referred to as a “spin-labeled ligand” [10]. However, while the reduction of the compounds $[(PR_3)_2(CO)_3(mpz)W](PF_6)$ seems to proceed in an apparently reversible one-electron fashion, the well-resolved EPR spectra of the thus-formed neutral radical

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species with $18 + \delta$ valence electron configuration revealed the loss of one triorganophosphane ligand [4,5]:



In previous work we have introduced the term “ $18 + \delta$ ” [11,12] for the valence electron configuration of the metal in paramagnetic carbonyl or related complexes where the organometallic complex fragment receives a small but EPR-detectable amount of unpaired electron density from coordinated reduced, i.e. anion radical, ligands [13]. We [11,12] and others [14] could show that this small effect of charge delocalization also results in a selective substitutional activation which can even be catalytic [11,12] (electron transfer catalysis [15]). Furthermore, the species which resulted from CO substitution by triorganophosphines are new donor/acceptor substituted metal carbonyl complexes with decreased frontier orbital energy gaps [11,16].

In this work we report on (a) the synthesis and comparative characterization of the molybdenum analogues $[(\text{PR}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}](\text{PF}_6)$ of the previously described [5] tungsten compounds, (b) electronic absorption data of the cationic complexes, including a study of the charge-determined solvatochromic behavior [17–19] of the well-soluble derivative $[(\text{PCy}_3)_2(\text{CO})_3(\text{CH}_3(\text{CH}_2)_{17}\text{-pz})\text{W}](\text{PF}_6)$ with a long pendant alkyl chain, and (c) and EPR, IR and UV-vis spectroelectrochemical approach to the reduction process (1) which implicates a further kind [12] of consequence following the creation of $18 + \delta$ electron species.

2. Results and discussion

2.1. Synthesis and characterization

The use of a long-chain *N*-alkyl-substituted pyrazinium ligand $\text{CH}_3(\text{CH}_2)_{17}\text{-pz}^+$ instead of mpz^+ [5] did not significantly change the synthetic and spectroscopic properties of the corresponding bis(tricyclohexylphosphine)tricarbonyltungsten(0) complex. The molybdenum analogues $[(\text{PR}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}](\text{PF}_6)$ of the previously reported [5] tungsten(0) complexes could be obtained by reacting the precursor complexes $(\text{PR}_3)_2(\text{CO})_3\text{Mo}$ [2] with *N*-methylpyrazinium hexafluorophosphate. Although the molybdenum compounds are more labile than the tungsten derivatives, they could be clearly identified by ^1H - and ^{31}P -NMR and by carbonyl vibrational spectroscopy in the infrared (see Section 4 and Table 4). In general, the complexes of the π electron rich 16 VE fragments $(\text{PR}_3)_2(\text{CO})_3\text{M}$ with the $\text{R}'\text{-pz}^+$ acceptor ligands are much more stable than compounds with stronger σ

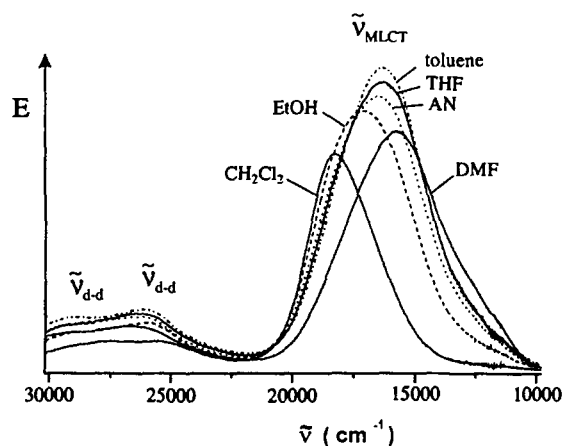
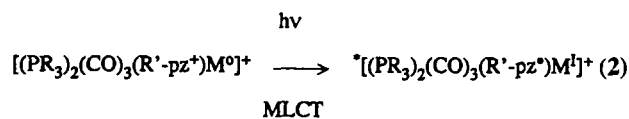


Fig. 1. Absorption spectra of $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$ in different solvents (absorbance scales different).

donor but weaker π acceptor ligands such as 4,4'-bipyridine [4], confirming the capability of these fragments to bind very weak σ bases via their π donor character [1,2].

2.2. Electronic absorption spectra and solvatochromism

The cationic complexes $[(\text{PR}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{M}]^+$ exhibit intense, usually deep-blue colors in the solid state and in solution. These colors are due to symmetry-allowed metal-to-ligand charge transfer (MLCT) transitions between the $4d_{xz}$ or $5d_{xz}$ orbital and the low-lying π^* MO of $\text{R}'\text{-pz}^+$. In addition to the long-wavelength MLCT band there are weak features around 400 nm (d–d or ligand–field transitions [4,5], Fig. 1).



The MLCT absorption maxima are summarized as a function of the solvent in Table 1. The lability of the molybdenum compounds and the poor solubility of tricyclohexylphosphine-containing complexes with the mpz^+ ligand limited the range of solvents, for less polar solvents we thus used the derivative $[(\text{PCy}_3)_2(\text{CO})_3(\text{CH}_3(\text{CH}_2)_{17}\text{-pz})\text{W}](\text{PF}_6)$ with a long pendant alkyl chain.

In comparison with the potentially very narrow long-wavelength MLCT bands ($\Delta\tilde{\nu}_{1/2}$ 900 cm^{-1}) of the neutral dinuclear compounds $[(\text{PR}_3)_2(\text{CO})_3\text{M}]_2(\mu\text{-pz})$, pz = pyrazine [4,5], the MLCT bandwidths of the cationic compounds presented here are in a rather “normal” range of 3000–5000 cm^{-1} (bandwidths $\Delta\tilde{\nu}_{1/2}$ at half-height). These intense ($\epsilon \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) bands not only show the familiar broadening in more “polar” solvents, they are also more solvatochromic than those

Table 1
MLCT absorption maxima $\tilde{\nu}_{\max}$ (cm^{-1}) of complexes $[(\text{PR}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{M}]\text{PF}_6$ in different solvents

Solvent	M R	Mo		W	
		$\tilde{\nu}_{\max}$ Pr ^a	$\tilde{\nu}_{\max}$ Cy ^a	$\tilde{\nu}_{\max}$ Pr ^a	$\tilde{\nu}_{\max}$ Cy ^{a,b}
Dichloromethane	0.00 ^d	16860	17360	18270	18180
1,2-Dichlorobenzene		16670			
Chlorobenzene		15620		17080	
Ethanol		15470		17130	
Nitrobenzene	0.21	15220	15460	16810	17080
Acetonitrile	0.36	15110	15170	16550	16830
Acetone	0.44	15000		16470	16230
Toluene		15000		16340 ^e	16230 ^f
Diethyl ether	0.49	14970			16690
<i>p</i> -Xylene		14910			
Benzene		14890		16340	
Mesitylene		14840		15960	
THF	0.52	14740	15020	16310	16420
DMF	0.80	14330 ^g	14200 ^g	15760	15850
DMSO	0.77	14190 ^g		15660	15820

^a R' = CH₃; ^b R' = (CH₂)₁₇CH₃; ^c from Refs. [17] and [20]; ^d DN value for 1,2-dichloroethane; ^e $\epsilon = 13500 \text{ M}^{-1} \text{ cm}^{-1}$; ^f $\epsilon = 9400 \text{ M}^{-1} \text{ cm}^{-1}$; ^g labile complexes.

of complexes $[(\text{PR}_3)_2(\text{CO})_3\text{M}]_2(\mu\text{-pz})$ [4]. However, there is also a qualitative difference. While the solvatochromic behavior of most [17–19] carbonylmetal complexes, including the dinuclear systems mentioned above [5], can be well-correlated with an established solvent parameter E_{MLCT}^* (which has been deduced from studies of $(\text{bpy})\text{M}(\text{CO})_4$, M = Cr, Mo, W [18]), the energies of the MLCT band maxima of the complex cations $[(\text{PR}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{M}^0]^+$ cannot be correlated with E_{MLCT}^* . However, the donor numbers (DN) [17,20] of the solvents used yield reasonable correlations, as in the case of $[(\text{PCy}_3)_2(\text{CO})_3(\text{CH}_3(\text{CH}_2)_{17}\text{-pz})\text{W}]^+$: $\tilde{\nu}_{\text{MLCT}} = 17900\text{--}2520 \text{ cm}^{-1} \times (\text{DN})$; correlation coefficient $r = 0.973$ (Fig. 2). The other complexes exhibit similar correlations with the DN parameter.

Although the electron accepting π system of metal-bound R'-pz⁺ is exposed to the solvent, the MLCT band

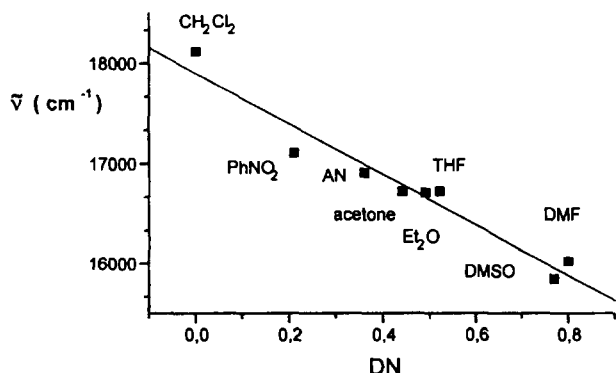


Fig. 2. Correlation of MLCT absorption maxima of $[(\text{PCy}_3)_2(\text{CO})_3(\text{CH}_3(\text{CH}_2)_{17}\text{-pz})\text{W}]\text{PF}_6$ with donor numbers (DN).

energies do not correlate with the solvent parameter $E_{\pi}(\text{CT})$ which had been obtained from the solvatochromism of complexes $(\text{CO})_5(\eta^2\text{-TCNE})\text{M}$, M = Cr, W [21]. Apparently, the solvatochromic behavior is dominated by interaction of the positive charge of the complexes with the (donor) solvent. This result demonstrates that the solvatochromism of MLCT bands of carbonylmetal compounds does not uniformly correlate with one specific parameter; unusual electronic and steric situations [21] or the occurrence of free charges [22] as shown here may alter the response of the MLCT transition energy to the environment. In the present case, the bathochromic shift with increasing donor character of the solvent indicates stronger stabilization of the MLCT excited state (2) by those solvents.

When comparing analogous molybdenum(0) and tungsten(0) complexes, the lower MLCT energy of the former is obvious (Table 1). As the electrochemical data will attest (see below, Table 2), the molybdenum complexes have a higher-lying HOMO (metal d orbital) and a slightly lower-lying (R'-pz⁺)-centered LUMO than the tungsten analogues. The differences between PⁱPr₃- and PCy₃-containing complexes of the same metal are less pronounced; the stronger donating PⁱPr₃ ligands cause a small destabilization of the HOMO (cf. Table 2) and thus a slight bathochromic shift of the MLCT bands (Table 1).

2.3. Cyclic voltammetry and spectroelectrochemistry

The *N*-alkylpyrazinium complexes $[(\text{PR}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{M}]\text{PF}_6$ undergo apparently reversible one-electron oxidation and reduction processes at rather close-lying potentials (Table 2) [5]. The thus-indicated relatively small HOMO–LUMO gap is also evident from the low-energy charge transfer transitions (Table 1).

Table 2
Electrochemical data^a from cyclic voltammetry

Complex	Solvent ^b	E_{ox}^c	E_{red1}^c	E_{red2}^d
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}]\text{PF}_6$	THF	+0.01	-1.16	-2.22
	CH ₃ CN	+0.08	-1.13	-2.05
$[(\text{PCy}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}]\text{PF}_6$	CH ₂ Cl ₂	+0.04	-1.23	-2.41
	THF	+0.06	-1.15	-2.23
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}]\text{PF}_6$	CH ₃ CN	+0.09	-1.15	-2.16
	CH ₂ Cl ₂	+0.22	-1.24	-2.21
$[(\text{PCy}_3)_2(\text{CO})_3(\text{mpz})\text{W}]\text{PF}_6$	THF	+0.08	-1.20	-2.17
	CH ₃ CN	+0.15	-1.18	-1.99
	CH ₂ Cl ₂	+0.27	-1.24	-2.28
$[(\text{PCy}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{W}]\text{PF}_6^c$	THF	+0.13	-1.20	-2.21
	CH ₃ CN	+0.17	-1.19	-2.04
	CH ₂ Cl ₂	+0.25	-1.24	-2.28
	DMF	+0.10	-1.18	-2.07
	CH ₃ CN	+0.35	-1.06	-1.98

^a Potentials in V vs. $\text{FeCp}_2^{+/0}$, 100 mV s^{-1} scan rate. ^b Containing 0.1 M Bu_4NPF_6 as electrolyte. ^c Redox potentials for reversible or quasireversible waves, peak potential differences 60–100 mV. ^d Cathodic peak potential for irreversible process. ^e R' = $(\text{CH}_2)_{17}\text{CH}_3$.

Associating the redox potential variations with changes in frontier orbital energies we observe a relative destabilization of the HOMO for the molybdenum species as evident from their more facile oxidation. There is also a slightly easier reduction of the molybdenum analogues in comparison with the tungsten derivatives, indicating a slightly lower LUMO level.

Employing an established approximation [23,24], we were able to compare electrochemically determined differences $\Delta E_{\text{red/ox}} = E_{\text{red}} - E_{\text{ox}}$, associated with the HOMO–LUMO energy differences in the relaxed state (energy potential minima), with the energies of the HOMO–LUMO transition (MLCT absorption). According to the Franck–Condon principle, the λ_{max} (nm) or E_{max} (eV) values correspond to vertical processes, i.e. to transitions between energy potential surfaces at the unchanged ground state geometry. The difference χ

$$E_{\text{max}} \text{ (in eV)} - \Delta E_{\text{red/ox}} \text{ (in V)} = \chi$$

thus includes contributions from intramolecular relaxation and solvent reorganization after MLCT excitation [23,24]. Using the data from Tables 1 and 2 and Eq. (3), the rather large values for χ between 0.65 and 0.74 (eV) for the complexes studied here are in agreement with the fairly high band widths (Fig. 1). Distinctly smaller values for χ are observed for neutral complexes [4] or more rigid chelate systems [24]; apparently, the strong specific solvation of the cations $[(\text{PR}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{M}]^+$ and their non-chelate structure allows for extensive reorganization on MLCT excitation.

The one-electron oxidation to M^{I} species (4) is reversible in the cyclic voltammetric experiment at about 100 mV s^{-1} scan rate [5], however, EPR, UV-vis and IR spectroelectrochemical studies reveal a rather rapid irreversible decomposition of the dicationic compounds. Both the expected bleaching of the MLCT band and the high-energy shift of the carbonyl stretching bands to about 2040 and 1940 cm^{-1} are compatible with a metal-centered oxidation [4,25], however, due to the lability of the dications they were not characterized further. The reduction to neutral species, however, is

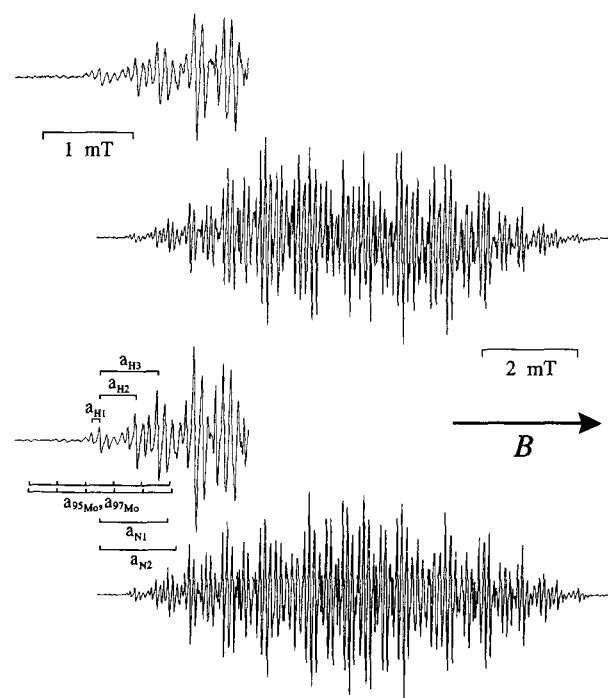
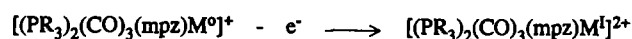


Fig. 3. EPR spectrum of $[(\text{P}^1\text{Pr}_3)(\text{CO})_3(\text{mpz})\text{Mo}]^\bullet$ as obtained by reduction of $[(\text{P}^1\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}](\text{PF}_6)$ with K in THF/0.01 M [2.2.2] cryptand. Spectrum with amplified low-field wing section (top) and computer simulation with the data from Table 3 and 0.025 mT line width (bottom).

spectroelectrochemically reversible in THF or dichloromethane, but less so in acetonitrile. The second reduction to anionic species is always irreversible; if pyrazine-localized, this process would result in the formation of an “antiaromatic” 8π electron compound [26].



Similarly to the previously described tungsten complex ($\text{R} = {}^1\text{Pr}$) [5], the corresponding one-electron reduced molybdenum compound yielded a well-resolved EPR spectrum which could only be analyzed assuming the coupling of only one ${}^{31}\text{P}$ nucleus with the unpaired electron (Fig. 3, Table 3).

Table 3
EPR data of methylpyrazinium radical complexes $[\text{X}(\text{mpz})^\bullet]$

X	Coupling constants a (μT) ^a						$\Delta a(\text{CH})$ ^b	$\Sigma a(\text{CH})$ ^b	g	Reference
	$\text{H}^{2,6}$	$\text{H}^{3,5}$	CH_3	N^1	N^4	X				
$(\text{NH}_3)_5\text{Ru}^{2+}$	387	< 180	723	683	870	580 ^c 650	> 270	< 567	2.0021	[9]
$(\text{CO})_5\text{W}$	386	154	714	784	870	n.d.	232	540	2.0051	[5]
$(\text{P}^1\text{Pr}_3)(\text{CO})_3\text{W}$	394	77	617	709	862	3235 ^d	317	471	2.0087	[5]
$(\text{P}^1\text{Pr}_3)(\text{CO})_3\text{Mo}$	409	87	646	738	846	2650 ^{d,e}	322	496	2.0041	This work
—	458	121	732	700	828	—	337	579	2.0034	[10]

^a $100 \mu\text{T} = 1 \text{ G}$ (gauss); assignments of $a(^{14}\text{N})$ uncertain. ^b Differences and sums of $a(\text{H}^{3,6})$ and $a(\text{H}^{3,5})$ (μT). ^c Metal hyperfine splitting $a(^{99}\text{Ru})$ and $a(^{101}\text{Ru})$. ^d $a(^{31}\text{P})$. ^e $a(^{95,97}\text{Mo}) = 315 \mu\text{T}$.

With $a > 2.5$ mT, the ^{31}P coupling constants are unusually large, since related radical complexes with *cis*-(PR_3) $_2(\text{CO})_3\text{M}$ and pyrazine or 4,4'-bipyridine radical anions have $a(^{31}\text{P}) < 1.5$ mT [16,27]. The other hyperfine splitting parameters of the neutral compounds are in full agreement with an $\text{M}^0(\text{R}'\text{-pz})^\cdot$ formulation, thus representing an application of ($\text{R}'\text{-pz}$) $^\cdot$ as spin-labeled ligands [10,13]. Whereas the relatively small sums $\Sigma a(\text{CH})$ of pyrazine ring proton coupling constant suggest some spin delocalization to the coordinated metal complex fragments, the large differences $\Delta a(\text{CH})$ reflect the asymmetry between the (PR_3) $_2(\text{CO})_3\text{M}-\text{N}$ and CH_3-N sites. The smaller ^{31}P coupling and g factor for the molybdenum analogue, as compared with the tungsten derivative, were similarly reported before [27]. Larger 5d orbitals and a higher spin-orbit coupling constant of tungsten are responsible for these effects. The $^{95,97}\text{Mo}$ isotope coupling is in a typical range for

Table 4
Carbonyl stretching frequencies from IR spectroelectrochemistry

Complex	Solvent	$\bar{\nu}_{\text{CO}}$ (cm^{-1})
$[(\text{PCy}_3)_2(\text{CO})_3(\text{mpz})\text{Mo}(\text{PF}_6)]^\cdot$	CH_2Cl_2	1988s, 1918s, 1866vs
$[(\text{PCy}_3)_3(\text{CO})_3(\text{mpz})\text{Mo}]^\cdot$	CH_2Cl_2	1926m, 1809vs, 1782sh
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}(\text{PF}_6)]^\cdot$	CH_2Cl_2	1984s, 1909s, 1861vs
$[(\text{P}^i\text{Pr}_3)_3(\text{CO})_3(\text{mpz})\text{W}]^\cdot$	CH_2Cl_2	1921m, 1801vs, 1772sh
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}(\text{PF}_6)]^\cdot$	THF	1973s, 1895s, 1855vs
$[(\text{P}^i\text{Pr}_3)_3(\text{CO})_3(\text{mpz})\text{W}]^\cdot$	THF	1925m ^a , 1806vs ^b , 1790sh
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}(\text{PF}_6)]^\cdot$	CH_3CN	1976s, 1896s, 1854vs
$[(\text{P}^i\text{Pr}_3)_3(\text{CO})_3(\text{mpz})\text{W}]^\cdot$	CH_3CN	1926m, 1807vs, 1771sh
$[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}]^{2+}$	CH_3CN	2044m, 1976s, 1948m
$[(\text{PCy}_3)_2(\text{CO})_3(\text{mpz})\text{W}(\text{PF}_6)]^\cdot$	CH_2Cl_2	1983s, 1907s, 1856vs
$[(\text{PCy}_3)_3(\text{CO})_3(\text{mpz})\text{W}]^\cdot$	CH_2Cl_2	1920m, 1796vs, 1773sh
$[(\text{PCy}_3)_2(\text{CO})_3(\text{mpz})\text{W}]^{2+}$	CH_2Cl_2	2037m, 1983s, 1938m
$[(\text{PCy}_3)_2(\text{CO})_3(\text{R}'\text{-pz})\text{W}(\text{PF}_6)]^\cdot$	CH_2Cl_2	1983s, 1907s, 1857vs
$[(\text{PCy}_3)_3(\text{CO})_3(\text{R}'\text{-pz})\text{W}]^\cdot$	CH_2Cl_2	1916m, 1795vs, 1771sh

^a Additional weak band at 1933 cm^{-1} (impurity formed after prolonged reduction). ^b Additional shoulder at 1818 cm^{-1} (impurity formed after prolonged reduction). ^c $\text{R}' = (\text{CH}_2)_{17}\text{CH}_3$.

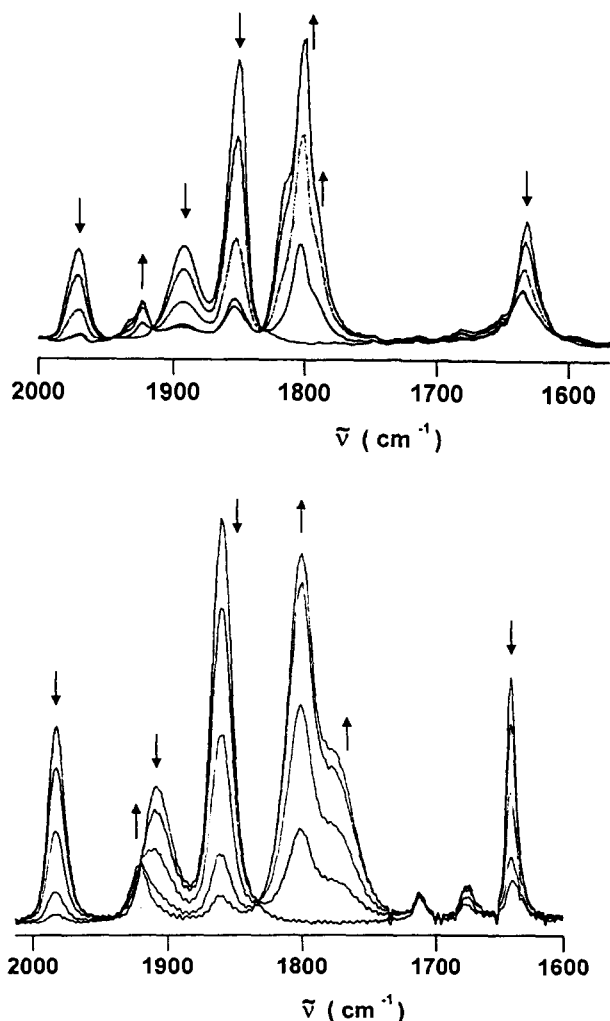


Fig. 4. IR spectroelectrochemistry (reduction) of $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}(\text{PF}_6)]^\cdot$ in THF/- (top) and $\text{CH}_2\text{Cl}_2/0.1\text{ M Bu}_4\text{NPF}_6$ (bottom). The shoulders at 1818 and 1933 cm^{-1} in THF are due to slow decomposition.

anion radical complexes of Mo^0 (d^6 configuration) [13,27].

Both the apparent loss of one phosphine ligand and the large ^{31}P coupling from the one remaining triorganophosphine group point to a different composition and structure of the neutral species as compared with the spectroscopically and structurally characterized [5] cations $[(\text{PR}_3)_2(\text{CO})_3(\text{mpz})\text{M}]^+$. Whereas the latter have a close to octahedral coordination arrangement, the EPR spectroscopically detected loss of one PR_3 ligand and the large remaining ^{31}P coupling suggest a different, most likely pentacoordinate structure, of what is assumed to be $[(\text{PR}_3)_3(\text{CO})_3\text{M}(\text{mpz})]^\cdot$.

To further support this assumption, we carried out IR spectroelectrochemical studies of several species in the carbonyl stretching region. Chemically reversible changes were observed (Fig. 4) which are listed in Table 4.

For the *trans,mer*-configured cations, there is a well-resolved three-band pattern for the tricarbonyl-metal moiety. On reduction (and EPR spectroscopically detected PR_3 dissociation), these bands shift as expected [25] to lower energies because of the decreasing π acceptor character of the non-innocent $\text{R}'\text{-pz}$ ligands after electron uptake. However, there is also a changed pattern with one high energy and two close-lying low-energy carbonyl stretching bands (Fig. 4, Table 4). Similar band patterns at similar wavenumbers have been observed for pentacoordinate tricarbonyl anions such as $[(\text{catecholate})\text{Mn}(\text{CO})_3]^-$ [28] or $[(\text{catecholate})\text{W}(\text{CO})_3]^{2-}$ [29]; it arises because of a nearly "facial" arrangement of carbonyl ligands, as in a distorted trigonal bipyramidal arrangement. The consequence of such an assumption is a close "cis" arrangement between the triorganophosphine and the alkylpyrazinium radical

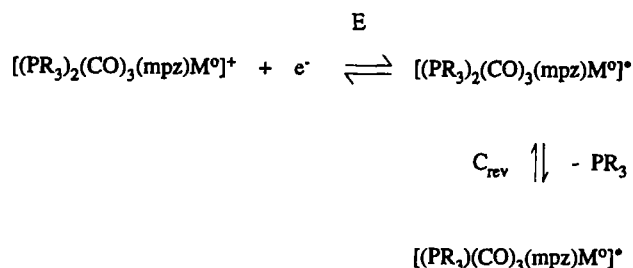
ligand which would explain the large ^{31}P hyperfine coupling [13].

On spectroelectrochemical reduction, the intense bands at about 1640 cm^{-1} (ring vibration) become weaker without significant shifting (Fig. 4). This observation suggests a more dipolar character of the cations as compared with the neutral radical complexes.

The system with the most stable reduction product, $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$, has been studied also by UV-vis spectroelectrochemistry. Fig. 5 shows the spectral response which consists of the expected [30] disappearance of the long-wavelength MLCT band and the emerging of a low-intensity broad band centered at 750 nm. This new feature is attributed to the mpz' intra-ligand SOMO \rightarrow LUMO transition ($\pi \rightarrow \pi^*$), which is symmetry-forbidden ($b_{1u} \rightarrow a_u$ [26]) unless the inversion symmetry is lifted by unsymmetrical coordination.

Compound $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$ was further used to confirm the identity of the reduced product obtained via spectroelectrochemistry and chemical reduction. Thus, the electrochemical reduction of this complex inside the EPR cavity produced the same spectrum as obtained by reduction with potassium, both reactions being carried out in THF [5]. Conversely, the radical complex as generated from reduction with potassium in THF/0.01 M [2.2.2]-cryptand gave the IR and UV-vis spectra identical to those reported above for the spectroelectrochemically prepared species. In addition the cyclic voltammogram of this species was identical to the one obtained for the non-reduced cationic complex. The reversible one-electron nature of the first reduction of $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$ was further checked by coulometry and a.c. polarography at 120 Hz. The electrochemically "normal" one-electron behavior can be reconciled with the spectroscopic results only by assuming a very rapid but reversible dissociation

of one of the two triorganophosphine ligands on reduction (EC_{rev} process [31]):



3. Summary

Based on all available evidence we must conclude, therefore, that the conversion of an mpz⁺ to an mpz' ligand causes the rapid reversible dissociation (5) of one of the bulky and electron-rich triorganophosphine ligands without subsequent addition of a solvent molecule to the first coordination sphere. The metal is thus assumed to be pentacoordinate in the reduced state. Such pentacoordination is not uncommon for d⁶ centers with highly π electron donating ligands; catecholate dianions in complexes with W⁰ [29] or Mn^I [28] and reduced 1,4-diazabutadienes in complexes with Cp⁺Ir^{III} [32] are other examples. The neutral methylpyrazinium radical must then be viewed as a π electron donor in contrast to the π accepting cation; via the $18 + \delta$ electron concept [11,12]. This redox-"Umpolung" leads to a ligand activation (dissociation) without replacement, i.e. substitution.

4. Experimental section

4.1. Syntheses

Although the solid products are rather stable towards exposure to air, all synthetic and spectroscopic manipulations were carried out under an argon atmosphere using dry solvents.

The starting materials $(\text{PR}_3)_2(\text{CO})_3\text{M}$ [2] and methylpyrazinium hexafluorophosphate $(\text{mpz})(\text{PF}_6)$ [5] and the tungsten complexes $[(\text{PR}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$, R = ⁱPr, Cy [5], were obtained according to literature procedures.

4.2. N-octadecylpyrazinium iodide

A mixture of 7.61 g (20 mmol) octadecyl iodide and 1.76 g (22 mmol) pyrazine was heated to reflux in 80 ml acetonitrile for 18 h. After cooling, pentane was added to produce two phases, stirring and subsequent

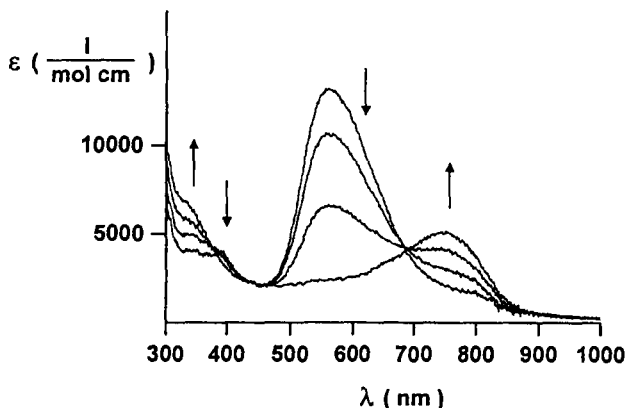


Fig. 5. UV-vis spectroelectrochemistry (reduction) of $[(\text{P}^i\text{Pr}_3)_2(\text{CO})_3(\text{mpz})\text{W}](\text{PF}_6)$ in THF/0.1 M Bu_4NPF_6 .

cooling to -18°C gave about 4 g of precipitate which was further purified by Soxhlet extraction (pentane, 72 h). Yellow shiny crystals were obtained in 29% yield (2.9 g). Anal. Found: C, 57.66; H, 9.06; N, 5.38%. $\text{C}_{22}\text{H}_{41}\text{IN}_2$ (460.5). Calc.: C, 57.38; H, 8.97; N, 6.08%. $^1\text{H-NMR}$ (CDCl_3): δ 0.86 (t, 3H, CH_3), 1.29 (m, 32H, $-\text{CH}_2-$), 2.07 (tt, 2H, NCH_2CH_2), 5.00 (t, 2H, NCH_2), 9.39 (d 2H, $\text{H}^{3,5}$), 9.44 (d, 2H, $\text{H}^{2,6}$).

4.3. *N*-octadecylpyrazinium hexafluorophosphate

Anion exchange was carried out by dissolving 2.9 g (6.3 mmol) of the iodide in 100 ml boiling water upon which 2.0 g (12.2 mmol) NH_4PF_6 were added. A precipitate formed and the cooling solution was treated with pentane to dissolve remaining impurities. Filtration and washing of the precipitate with pentane and water yielded an off-white material which was dissolved in acetonitrile and extracted repeatedly with pentane. Eventually, the almost colorless acetonitrile phase was dried with sodium sulfate and the solvent removed under vacuum. The colorless powder obtained in 83% yield (2.5 g) is soluble in acetonitrile. Anal. Found: C, 55.37; H, 8.54; N, 5.68%. $\text{C}_{22}\text{H}_{41}\text{F}_6\text{N}_2\text{P}$ (478.5). Calc.: C, 55.22; H, 8.64; N, 5.85%. $^1\text{H-NMR}$ (CD_3CN): δ 0.88 (t, 3H, CH_3), 1.31 (m, 32H, $-\text{CH}_2-$), 2.10 (tt, 2H, NCH_2CH_2), 4.55 (t, 2H, NCH_2), 8.69 (d 2H, $\text{H}^{3,5}$), 9.39 (d, 2H, $\text{H}^{2,6}$). UV (acetonitrile): λ_{max} 312(sh), 272 nm.

4.4. *trans,mer*-bis(triisopropylphosphine)(*N*-methylpyrazinium)tricarbonylmolybdenum(0) hexafluorophosphate

A suspension of 0.65 g (1.29 mmol) $(\text{P}^i\text{Pr}_3)_2(\text{CO})_3\text{Mo}$ and 0.311 g (1.30 mmol) $(\text{mpz})(\text{PF}_6)$ in 10 ml toluene were stirred for about 4 h at ambient temperature. The dark-blue precipitate was collected by filtration, washed with toluene and dried under vacuum. The yield was 0.86 g (90%). Anal. Found: C, 41.03; H, 6.56; N, 3.88%. $\text{C}_{26}\text{H}_{49}\text{F}_6\text{MoN}_2\text{O}_3\text{P}_3$ (740.5). Calc.: C, 42.17; H, 6.67; N, 3.78%. $^1\text{H-NMR}$ (CDCl_3): δ 1.5 (m, 36H, CCH_3), 2.49 (m, 6H, PCH), 2.94 (s, 3H, NCH_3), 6.37 (d 2H, $\text{H}^{2,6}$), 8.11 (d, 2H, $\text{H}^{3,5}$); $^3\text{J}(\text{HCCP}) = 13.5$ Hz, $^3\text{J}(\text{H}^2\text{H}^3/\text{H}^5\text{H}^6) = 4.7$ Hz, $^3\text{J}(\text{HCCH}_3) = 7.2$ Hz, $^{31}\text{P-NMR}$ (CDCl_3): δ -143.9 (sept, PF_6 ; $^1\text{J}(\text{PF}) = 713$ Hz), 51.2 (s, P^iPr_3). IR (CH_2Cl_2): $\tilde{\nu}$ 1986, 1916, 1867, 1633 cm^{-1} .

4.5. *trans,mer*-bis(tricyclohexylphosphine)(*N*-methylpyrazinium)tricarbonylmolybdenum(0) hexafluorophosphate

A suspension of 0.658 g (0.89 mmol) $(\text{PCy}_3)_2(\text{CO})_3\text{Mo}$ and 0.220 g (0.92 mmol) $(\text{mpz})(\text{PF}_6)$ in 10 ml toluene was stirred for about 4 h at ambient tempera-

ture. The dark-blue precipitate was collected by filtration, washed with few ml of toluene and dried under vacuum. The yield was 0.66 g (76%). Anal. Found: C, 50.49; H, 7.04; N, 3.39%. $\text{C}_{44}\text{H}_{73}\text{F}_6\text{MoN}_2\text{O}_3\text{P}_3$ (980.9). Calc.: C, 53.88; H, 7.50; N, 2.86%. $^1\text{H-NMR}$ (CDCl_3): δ 1.17–2.12 (m, 60H, CH_2), 2.14 (m, 6H, PCH), 2.92 (s, 3H, NCH_3), 6.42 (d 2H, $\text{H}^{2,6}$), 8.10 (d, 2H, $\text{H}^{3,5}$). $^3\text{J}(\text{H}^2\text{H}^3/\text{H}^5\text{H}^6) = 4.8$ Hz. $^{31}\text{P-NMR}$ (CDCl_3): δ -143.8 (sept, PF_6 ; $^1\text{J}(\text{PF})$ -713 Hz), 39.7 (s, PCy_3).

4.6. *trans,mer*-bis(tricyclohexylphosphine)(*N*-octadecylpyrazinium)tricarbonyltungsten(0) hexafluorophosphate

This compound was synthesized in an analogous fashion as described previously [5], using *N*-octadecylpyrazinium hexafluorophosphate in toluene. The deep-blue complex was obtained in 83% yield. Anal. Found: C, 55.80; H, 8.17; N, 1.90%. $\text{C}_{61}\text{H}_{107}\text{F}_6\text{N}_2\text{O}_3\text{P}_3\text{W}$ (1307.3). Calc.: C, 56.05; H, 8.25; N, 2.15%. $^1\text{H-NMR}$ (CD_3CN): δ 0.89 (t, 3H, CH_3), 1.28–1.91 (m, 90H, $-\text{CH}_2-$ and Cy), 2.12 (m, 2H, NCH_2CH_2), 2.33 (m, 6H, PCH), 2.84 (t, 2H, NCH_2), 6.76 (d, 2H, $\text{H}^{2,6}$), 8.53 (d, 2H, $\text{H}^{3,5}$); $^3\text{J}(\text{H}^2\text{H}^3/\text{H}^5\text{H}^6) = 5.56$ Hz.

4.7. Instrumentation

EPR spectra were recorded in the X-band on a Bruker System ESP 300E equipped with a Bruker ER035M Gaussmeter and a HP 5350B microwave counter. NMR spectra were taken on Bruker AM 200 and AC 250 spectrometers, IR spectra were obtained using a Bruker IFS 60 CS and Perkin-Elmer 684 and 283 instruments. UV-vis/NIR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in dry solutions of THF, dichloromethane or acetonitrile containing 0.1 M Bu_4NPF_6 , using a three-electrode configuration (glassy carbon electrode, Pt counter-electrode Ag/AgCl reference) and a PAR 273 potentiostat and function generator. A.c. polarography was performed using a PAR 263 potentiostat connected to a PAR 5209 lock-in amplifier. The ferrocenium/ferrocene couple $\text{Fc}^{+/0}$ served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell [33] for IR and UV-vis spectra and a two-electrode capillary for EPR studies [34].

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