Spectroelectrochemical Characterization of a Pyrazine-bridged Mixed-valent ($4d^5/4d^6$) Organometallic Analogue of the Creutz–Taube Ion

Wolfgang Bruns,[a] Wolfgang Kaim*[a] Eberhard Waldhör[a] and Michael Krejčik[b]

[a] *Institut für Anorganische Chemie der Universität, Pfaffenwaldring 55, D-70550 Stuttgart, Germany*
[b] *J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czech Academy of Sciences, Dolejškova 3, CZ-182 23 Prague, Czech Republic*

The dinuclear complex ion *trans,mer*-$[(PPr^i_3)_2(CO)_3Mo(\mu\text{-pz})Mo(CO)_3(PPr^i_3)_2]^+$ (pz = pyrazine), the closest yet reported organometallic analogue of the Creutz–Taube ion $[(NH_3)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$, has been characterized as a fully delocalized $Mo^{0.5}/Mo^{0.5}$ system by electrochemistry, EPR, electronic and vibrational absorption spectroscopy.

Investigations of the Creutz–Taube ion $[(NH_3)_5Ru^{III}(\mu\text{-pz})Ru^{II}(NH_3)_5]^{5+}$ **1** and of related d^5/d^6 mixed-valent systems have been enormously fruitful for the understanding of electron transfer and charge delocalization phenomena.[1,2] Attempts to produce similarly pyrazine-bridged organometallic d^5/d^6 analogues less susceptible to charge trapping by the solvent have long been unsuccessful because corresponding dinuclear complexes of $M(CO)_5$ fragments, M = Cr, Mo, W, are only irreversibly oxidized at high potentials.[3,4] Pyrazine-bridged dimers of the $(C_5R_5)(CO)_2Mn$ fragments, on the other hand, suffer from a pronounced dissociative lability, which is caused by a small ligand-field splitting.[4]

In the course of studies of the H_2-coordinating ability of $W(CO)_3(PR_3)_2$ fragments[5] we have prepared the dinuclear pyrazine complex *trans,mer*-$[(PPr^i_3)_2(CO)_3W(\mu\text{-pz})W(CO)_3(PPr^i_3)_2]$ **2** which exhibits facile oxidation to a stable and isolable W^I/W^0 mixed-valent cation **2**$^+$ the characteristics of which were described recently.[6]

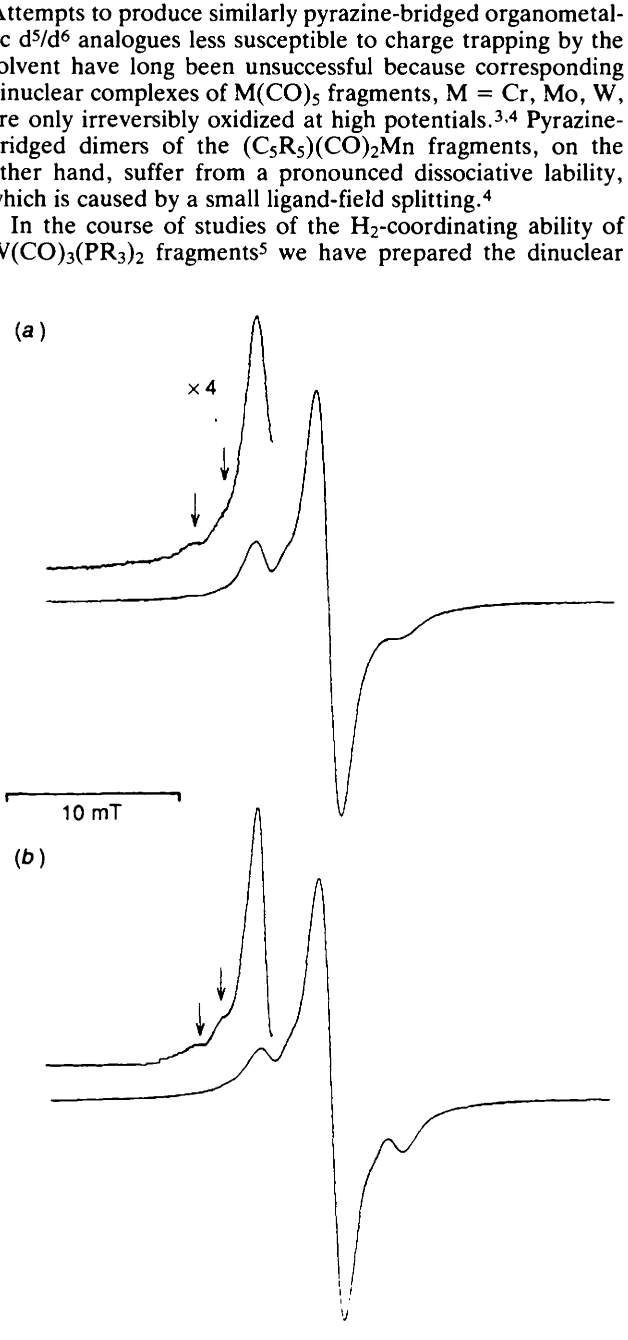


Fig. 1 EPR spectrum (*a*) of 3^+ at 298 K in CH_2Cl_2 ($\langle g \rangle$ 2.0438) with $^{95,97}Mo$ hyperfine coupling of 1.52 mT, the arrows indicate satellite lines from the combination with two equivalent magnetically active nuclei. (*b*) Computer simulated spectrum.

For an even closer approach to the Creutz–Taube ion **1** with its formally $4d^5/4d^6$ mixed-valent formulation we now report results on the Mo^I/Mo^0 analogue of **2** and **2**$^+$, *i.e.* on compound **3** and spectroelectrochemically generated **3**$^+$.

Complex **3** was synthesized from $Mo(CO)_3(PPr^i_3)_2$[5] and pyrazine in toluene.† Despite the higher dissociative lability of the molybdenum system **3**/**3**$^+$ as compared with the tungsten analogues **2**/**2**$^+$, two electrochemically reversible one-electron oxidation processes were observed at +0.01 and −0.37 V *vs.* $FeCp_2^{0/+}$ in THF–0.1 mol dm^{-3} Bu_4NClO_4. As in the Ru *vs.* Os series,[1,7] the $4d^5/4d^6$ system **3**$^+$ thus exhibits a smaller stability constant $K_c = [d^5/d^6]^2/[d^5/d^5]\cdot[d^6/d^6] = 10^{\Delta E/59\ \mathrm{mV}} = 10^{6.4}$ than the analogous $5d^5/5d^6$ system **2**$^+$ ($K_c = 10^{8.5}$) under the same conditions. Spectroelectrochemistry[8] of **3**$^+$ in CH_2Cl_2–0.1 mol dm^{-3} Bu_4NPF_6 showed an intense (ε *ca.* 7×10^3 mol^{-1} dm^3 cm^{-1}), relatively narrow ($\Delta\tilde{\nu}_{1/2}$ 700 cm^{-1}) symmetrical band at 2150 nm (4650 cm^{-1}) in the IR region.[6c] Depending on the classification[9] this band can be assigned to an intervalence transition ($Mo^0 \rightarrow Mo^I$, localized model) or a $\pi \rightarrow \pi^*$ transition between delocalized molecular orbitals.

In contrast to the situation for the Creutz–Taube ion **1** where the question of (de)localization has long been controversially discussed owing to lack of good experimental

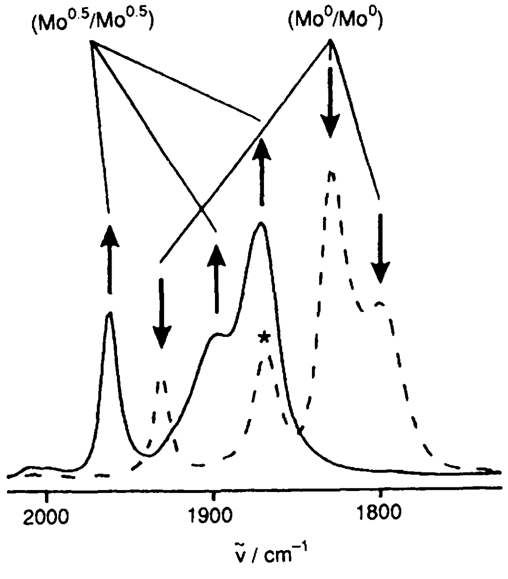
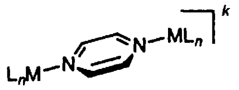


Fig. 2 IR spectra from oxidative spectroelectrochemistry of **3** ($\rightarrow$ **3**$^+$: 1962, 1898 and 1871 cm^{-1}) in CH_2Cl_2–0.1 mol dm^{-3} Bu_4NPF_6. The marked (*) band is that of $Mo(CO)_4(PPr^i_3)_2$ which is slowly formed from non-oxidized **3** in solution (see ref. 5).

---

† Dark-green compound [λ_{max} 867 nm, $\tilde{\nu}$(CO) 1932, 1829 and 1801 cm^{-1} in CH_2Cl_2], correct elemental analysis (C, H, N).



1; k = 5+, ML$_n$ = Ru(NH$_3$)$_5$
2; k = 0, ML$_n$ = W(CO)$_3$(P^{i}Pr$_3$)$_2$
2$^+$; k = 1+, ML$_n$ = W(CO)$_3$(P^{i}Pr$_3$)$_2$
3; k = 0, ML$_n$ = Mo(CO)$_3$(P^{i}Pr$_3$)$_2$
3$^+$; k = 1+, ML$_n$ = Mo(CO)$_3$(P^{i}Pr$_3$)$_2$

criteria[1,2] the organometallic species **3**$^+$ offers two convenient lines of evidence for full delocalization. First, the EPR signal of **3**$^+$ in CH_2Cl_2 solution at 298 K shows the presence of the coupling of one electron with two equivalent Mo nuclei (Fig. 1; ^{95}Mo: 15.72% natural abundance, I = 5/2; ^{97}Mo: 9.46%, I = 5/2). Both sets of satellite lines from the combinations with one (37.7%) and two magnetically active ^{95,97}Mo nuclei (6.3%) are observed (Fig. 1). Most significantly,[10a] the ^{95,97}Mo coupling constant of 1.52 mT is only about half the 2.6 mT for the corresponding mononuclear Mo^{I} complex [(PPr$^i_3$)$_2$(CO)$_3$Mo(pz)]$^-$. In glassy frozen dichloromethane, an axial EPR spectrum is obtained with $g_{\parallel}$ 1.9755 and $g_{\perp}$ 2.0655; anisotropic hyperfine coupling constants could not be determined with certainty.

Vibrational spectroscopy with an even shorter time window (*ca.* 10^{-12} s) than EPR (*ca.* 10^{-8} s) shows the expected high energy shifts of CO stretching bands upon oxidation, however, there is only one set of three shifted bands for the meridional CO groups in **3**$^+$ (Fig. 2).

The molybdenum system **3**$^+$ thus shows similar clear-cut evidence for a delocalized M$^{0.5}$/M$^{0.5}$ ground state (Class IIIA behaviour[9]) as the tungsten system **2**$^+$;[6] in contrast, a recent report[11] for a Mn^{II}/Mn^{I} carbonyl system showed partial valence trapping *via* the CO stretching band pattern. Summarizing, we have extended the small number of Mo^{I}/Mo^{0} mixed-valent dimers[10] by an example that bears structural as well as spectroscopic resemblance to the prototypical Creutz–Taube ion.

Support from DFG (SFB 270 and Exchange Program with CAV) is gratefully acknowleged.

Received, 21st July 1993; Com. 3/04329K

References

1 (*a*) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086; (*b*) P. A. Lay, R. H. Magnuson and H. Taube, *Inorg. Chem.*, 1988, **27**, 2364; (*c*) C. Creutz, *Progr. Inorg. Chem.*, 1983, **30**, 1.

2 *Mixed Valency Systems—Applications in Chemistry, Physics and Biology*, ed., K. Prassides, NATO ASI Series, 1991, C343.

3 (*a*) K. H. Panell and R. Iglesias, *Inorg. Chim. Acta*, 1979, **33**, L161; (*b*) A. J. Lees, J. M. Fobare and E. F. Mattimore, *Inorg. Chem.*, 1984, **23**, 2709.

4 (*a*) R. Goss and W. Kaim, *Inorg. Chem.*, 1986, **25**, 498; (*b*) W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov and E. K. H. Roth, *J. Am. Chem. Soc.*, 1992, **114**, 5693.

5 H. J. Wasserman, G. J. Kubas and R. R. Ryan, *J. Am. Chem. Soc.*, 1986, **108**, 2294.

6 (*a*) W. Bruns and W. Kaim, *J. Organomet. Chem.*, 1990, **390**, C45; (*b*) W. Bruns and W. Kaim in ref. 2, p. 365; (*c*) W. Kaim, W. Bruns, J. Poppe and V. Kasack, *J. Mol. Struct.*, 1993, **292**, 221; (*d*) See also W. Bruns, H.-D. Hausen, W. Kaim and A. Schulz, *J. Organomet. Chem.*, 1993, **444**, 121.

7 W. Kaim and V. Kasack, *Inorg. Chem.*, 1990, **29**, 4696.

8 M. Krejcik, M. Danek and F. Hartl, *J. Electroanal. Chem.*, 1991, **317**, 179.

9 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

10 (*a*) A. Das, J. C. Jeffery, J. P. Maher, J. A. McCleverty, E. Schatz, M. D. Ward and G. Wollermann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1515 and *Inorg. Chem.*, 1993, **32**, 2145; (*b*) C. J. Casewit and M. C. Rakowski DuBois, *Rev. Inorg. Chem.*, 1988, **9**, 199; (*c*) C. G. Young, *Coord. Chem., Rev.*, 1989, **96**, 89.

11 C. G. Atwood, W. E. Geiger and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 5310.