Notes

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Cis and Trans Isomers of $W(N_2)_2(PMe_2Ph)_4$[1]

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Introduction

The recent finding[4] that in the synthesis of known *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ the previously unreported trans isomer was also formed and that the isomers could be separated prompted us to investigate the analogous tungsten system. We wish to describe the effective separation of the cis and previously unreported trans isomers of $[W(N_2)_2(PMe_2Ph)_4]$.

Experimental Section

All manipulations were carried out under an inert atmosphere with standard Schlenk techniques[5] and a Vacuum Atmospheres Corp. drybox. Solvents were dried by standard procedures and distilled under dry dinitrogen prior to use. Infrared spectra were recorded using an Analect RFX-65 FTIR spectrometer. ^{31}P NMR spectra were recorded in C_6D_6 on a VXR-200 spectrometer operating at 80.984 MHz. Chemical shifts are referenced to PPh_3 (−5.8 ppm vs 85% H_3PO_4 = 0.0 ppm). $[WCl_4(PMe_2Ph)_2]$ was prepared according to a published procedures,[6] and WCl_6 was purchased from Aldrich Chemical Co. and used as received.

Preparation of *cis*- and *trans*-$[W(N_2)_2(PMe_2Ph)_4]$. Into a 250-mL Fischer Porter bottle was placed THF (75 mL), 1.03 g (7.46 mmol) of PMe_2Ph, 150 g (65.2 mmol) of 1% sodium amalgam, and a magnetic stirbar. After the mixture was stirred for ca. 5 min, WCl_6 (0.95 g, 2.4 mmol) was sprinkled onto the surface of the solution while stirring was maintained. An orange suspension formed immediately. The bottle was pressurized with N_2 (80 psi) and allowed to stir (16 h). After the bottle was depressurized, the red-brown solution was decanted and filtered through diatomaceous earth (acid washed) and washed with THF. Solvent was removed in vacuo to afford an oil. The oil was extracted with Et_2O (3 × 25 mL) and filtered. A brown solid (mainly cis isomer) remained. The combined filtrate was evaporated to dryness in vacuo to yield an oil (mixture of cis and trans isomers). The oil was stirred with pentane (50 mL) for 1 h. The solution was filtered to give a dirty yellow solid and a bright red-orange filtrate.

Solvent was evaporated from the filtrate and methanol (10 mL) added to the oil. After the mixture was cooled to 0 °C for 15 min, it was triturated and then stirred for 1 h to afford the pure trans isomer as a red-orange microcrystalline solid. The solid was filtered off, washed with cold methanol (5 mL), and dried in vacuo to yield 0.221 g (0.28 mmol, 11.7%). Anal. Calcd for $C_{32}H_{44}N_4P_4W$: C, 48.50; H, 5.59; N, 7.06. Found: C, 48.73; H, 5.72; N, 6.90. IR (KBr): $\nu(N_2)$ 1990 (m), 1898 (vs) cm^{-1}. ^{31}P NMR: trans, δ -21.28 (s, J_{PW} = 314.97 Hz).

The combined cis-isomer portions were dissolved in benzene (10 mL), and the solution was filtered. Methanol (80 mL) was added slowly to the filtrate with stirring. The mixture was cooled to 0 °C for 0.5 h to produce the dark yellow microcrystalline cis isomer. The product was filtered off, washed with methanol, and dried in vacuo to yield 0.815 g (1.03 mmol, 43.3%). Anal. Calcd for $C_{32}H_{44}N_4P_4W$: C, 48.50; H, 5.59; N, 7.06. Found: C, 48.43; H, 5.52; N, 6.87. IR (KBr): $\nu(N_2)$ 1991 (vs), 1913 (vs) cm^{-1}. ^{31}P NMR (A_2X_2): cis, δ -21.0 (t, 2, $J_{P_AP_X}$ = 5.74 Hz, J_{PW} = 313.05 Hz), −20.17 (t, 2, J_{PW} = 316.65 Hz).

Similar results were obtained using $[WCl_4(PMe_2Ph)_2]$. When pressures of N_2 greater than 80 psi were employed, reactions were carried out in a 300-mL Parr minireactor.

Electrochemistry. Cyclic voltammetry and potential-step experiments were carried out in a two-compartment, three-electrode cell fitted with a Luggin probe (connected to a silver pseudoreference electrode) using a Hi-Tek potentiostat, type DT2101, and Chemical Electronics (Birtley) Ltd. wave form generator, type 01, a Philips PM8041 X-Y recorder, and a Datalab type DL901 transient recorder. The cell was fitted with a platinum-wire or -disk working electrode, a tungsten secondary electrode, and a silver-wire pseudoreference electrode. The electrolyte was 0.2 M $[NBu^n_4][BF_4]$ in THF solution. Potentials quoted are referenced to the ferrocenium–ferrocene (Fc^+/Fc) couple = 0.00 V (0.535 V versus the SCE in this electrolyte). Kinetics experiments were carried out in a light-tight box, and the temperature was maintained at ±1 °C with a constant-temperature water bath as described previously.[7] Temperatures were monitored with a digital thermometer.

Results and Discussion

Reduction of either WCl_6 or $[WCl_4(PMe_2Ph)_2]$ with sodium amalgam in THF in the presence of ca. 90% of the stoichiometric amount of PMe_2Ph under varying pressures of N_2 led to the synthesis and separation of *cis*- and *trans*-$[W(N_2)_2(PMe_2Ph)_4]$. The presence of the two isomers was noted in the IR and ^{31}P NMR spectra of the crude reaction mixture. The tungsten isomers have different solubilities in pentane, as do their molybdenum analogues,[4] and this provided the basis for separation.

In experiments using WCl_6, values of the ratio of trans to cis isomers were determined at N_2 pressures ranging from 7 to 1000 psi. At 7 psi the ratio was ca. 1:4 and continued to increase to ca. 1:1 at 500 psi. However, between 500 and 1000 psi the ratio decreased to ca. 2:3. Some variation in the ratio was noted between different batches of WCl_6, and some variation is to be expected with the rate of stirring of this three-phase system.

The molybdenum cis and trans isomers are not completely separable because they slowly interconvert, and this complicates studies of their discrete properties. In contrast, no interconversions are observed with the tungsten isomers even after refluxing in benzene for 5 h. Thus, for the first time, both cis and trans isomers of a bis(dinitrogen) complex can be studied independently.

We find that the trans isomer is substitutionally inert. In contrast, one dinitrogen ligand in the tungsten cis isomer can be substituted by phenyl cyanide via a rate-determining dissociative pathway involving a five-coordinate intermediate: the cis-substituted product, $[W(N_2)(PhCN)(PMe_2Ph)_4]$, has been isolated.[8] In the presence of N_2 rather than PhCN, the trans isomer is *not* formed: this means that the five-coordinate intermediate is stereochemically rigid. Evidently the stereochemistry of $[W(N_2)_2(PMe_2Ph)_4]$ in the synthesis is set before the final N_2 ligand binds.[9]

Cyclic voltammetry shows that the trans tungsten isomer undergoes a fully reversible one-electron oxidation in the THF electrolyte at 0 °C, the reversibility of which is only marginally diminished at 25 °C. The cis isomer behaves in an analogous fashion except that the process is considerably less reversible (see Figure 1). At a scan rate of 0.30 V s^{-1}, i_{pc}/i_{pa} was 0.85 (trans) and 0.60 (cis) at 25 °C and 0.97 (trans) and 0.88 (cis) at 0 °C, respectively. The primary oxidation potentials of the two isomers are indistinguishable and occur at −0.83 V versus the ferrocenium–ferrocene couple. This value is essentially the same as those

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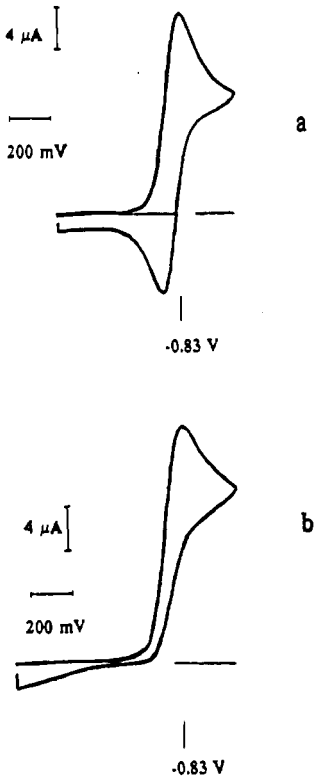

Figure 1. Cyclic voltammogram for the oxidation of (a) *trans*-[W-$(N_2)_2(PMe_2Ph)_4$] and (b) *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ in THF–0.2 M $[Bu^n_4][BF_4]$ at 100 mV s^{-1} and 25 °C. Peak potentials are referenced vs the ferrocenium/ferrocene couple.

measured for their molybdenum counterparts. A close correspondence of the redox potentials for isostructural molybdenum and tungsten 18e/17e couples is common.[9,10]

The redox potentials of closely related isomeric cis and trans pairs of these metals frequently differ by 200 or 300 mV. For example, the oxidation potential of *cis*-$[W(CO)_2(dppe)_2]$ is 310 mV positive of its trans isomer:[11,12] this contrasts sharply with the identical oxidation potentials measured for the cis and trans bis(dinitrogen) complexes. Whereas the relative energies of the HOMO's in the bis(carbonyl) isomers must differ significantly given the ca. 30 kJ mol^{-1} difference in their redox energies, it is evident that the HOMO's of the cis and trans bis(dinitrogen) complexes of molybdenum and tungsten are essentially isoenergetic. This is at variance with theoretical calculations based upon the model compounds *cis*- and *trans*-$[Mo(N_2)_2(PH_3)_4]$ which suggest the relative energies of the HOMO's differ by ca. 48 kJ mol^{-1}.[13] However, it has been predicted that the oxidation potentials for low-spin, octahedral d^6 *cis*- and *trans*-$[ML_4L'_2]$ isomers, where L is a better π-acceptor than L′, should be the same.[14] There is ample evidence that a phosphine such as PMe_2Ph is a better π-acceptor than N_2. In cases where the phosphine is small enough, it will coordinate to molybdenum in the zero oxidation state in place of N_2. For example, (i) reduction of a $[MoCl_3(THF)_3]/PH_2Ph$ mixture with Na/Hg under N_2 afforded $[Mo(PH_2Ph)_6]$[15] and (ii) reduction of a $[MoCl_3(triphos)]/PMe_2Ph$ mixture, where triphos = $PhP(CH_2CH_2PPh_2)_2$, with Na/Hg under N_2 yielded *fac*-$[Mo(N_2)(triphos)(PMe_2Ph)_2]$.[16] Displacement of N_2 from *cis*-$[Mo(N_2)_2(PMe_3)_4]$ by PMe_3 produced $[Mo(N_2)(PMe_3)_5]$.[17]

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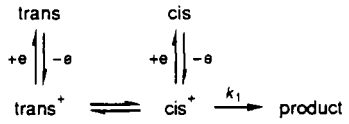
Scheme I



We have considered the possibility that an alternative interpretation of the cyclic voltammetry is that E°_{app} (app = apparent) has been determined rather than E° values for the cis/cis$^+$ and trans/trans$^+$ couples. This could arise, for example, if the cis cation is rapidly and extensively converted to the trans cation by isomerization or by a cross-reaction (see Scheme I). It is then possible that E°_{app} for the cis isomer could have a value close to that of E°_{trans} but substantially negative of E°_{cis}. However, if such an interpretation were valid, then one would expect the apparent reversibility of both systems to be essentially the same at all scan rates. This is clearly not the situation as is evident from Figure 1: rapid and extensive conversion of cis$^+$ to trans$^+$ does not occur on the time scale of the experiment, but rather the cis cation is removed by a following chemical reaction.

We have also considered the possibility that E_p(cis) might be substantially shifted from its reversible value by fast following chemistry. The k_1 for the loss of N_2 from the cis cation was determined by a single-potential-step method as discussed below. At 25 °C k_1 is ca. 2.7 s^{-1}. This is insufficient to give a significant shift in the peak potential relative to that for a fully reversible system; at a scan rate of 100 mV s^{-1} we calculate this shift to be less than 4 mV.

A particularly important aspect of the chemistry of *cis*- and *trans*-bis(dinitrogen) compounds of molybdenum and tungsten in their 0 and +1 oxidation states is the relative rate of loss of an N_2 ligand. This bears upon substitution reactions and, of particular importance, the formation of N–C bonds with alkyl halides (RX), which occurs via the following sequence: N_2 loss, homolytic cleavage of RX, and attack by R• on the Mo(I) or W(I) dinitrogen intermediates.[18] The rate of dissociation of N_2 is greater (i) from molybdenum than from tungsten, (ii) from cis compounds than trans compounds, and (iii) from Mo(I) or W(I) than from their Mo(0) and W(0) counterparts.

A direct comparison of the rate of dissociation of N_2 from cis and trans compounds of tungsten in their 0 and +1 oxidation states can now be made for a set of compounds possessing the same ligands.

The rate of dissociation of N_2 from molybdenum and tungsten bis(dinitrogen) complexes can be measured by monitoring their substitution reaction with ligands such as PhCN under pseudo-first-order conditions in the dark. The rate constant, k_1, for dissociation of N_2 from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ is 6.4×10^{-5} s^{-1} at 300 K (eq 1).[7] Under the same conditions the dissociation

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{10^5 k_1 = 6.4\ s^{-1}} [W(N_2)(PMe_2Ph)_4] + N_2 \quad (1)$$

$$trans\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{k_1 \le 10^{-9}\ s^{-1}} [W(N_2)(PMe_2Ph)_4] + N_2 \quad (2)$$

of N_2 from *trans*-$[W(N_2)_2(PMe_2Ph)_4]$ is immeasurably slow. We put an upper limit on the value of k_1 (eq 2) to be $\le 1 \times 10^{-9}$ s^{-1}. This parallels the behavior of *trans*-$[W(N_2)_2(dppe)_2]$.[18] The trans effect is clearly dominant in determining the lability of the W–N_2 bond: N_2 trans to a tertiary phosphine is at least 5 orders of magnitude more labile than when trans to N_2.[8]

The rate of loss of N_2 from molybdenum(I) and tunsten(I) bis(dinitrogen) complexes can be measured by potential-step methods[19] in which the cation is generated from the Mo(0) or W(0) precursor. The value of k_1 for bis(dinitrogen) complexes

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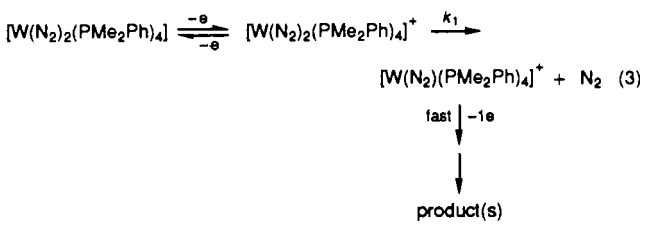
of Mo and W has been determined previously by a double-potential-step method.[7] For the cis and trans monodentate phosphine complexes studied here, the rate-determining loss of N_2 from the 17e cation is followed by fast one-electron oxidation chemistry (eq 3). We therefore determined k_1 by a single-potential-step



method.[20] The value of k_1 for N_2 loss from the cis cation was estimated to be 2.7 (±0.5) s^{-1} and for the trans cation to be 0.51 (±0.04) s^{-1} at 298 K. The rate of N_2 loss from the cis cation is ca. 5 orders of magnitude faster than for the neutral complex, and the corresponding difference for the trans isomer is at least 8 orders of magnitude. Whereas the trans effect appears to dominate the relative lability of N_2 in the metal(0) isomers, the difference in relative rates of N_2 loss from the isomers in the +1 oxidation state is considerably less dramatic (ca. a factor of 5). In the higher oxidation state the ligand arrangement appears less important in determining the lability of the N_2 ligand.

The temperature dependence of the rate constants was determined in order to calculate activation parameters. The $\Delta H^{\ddagger}$ (kJ mol^{-1}) and $\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}) values (with estimated errors in parentheses) for *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ are 98 (14) and +51 (51), and 109 (8) and +38 (24).[7] The corresponding values for *cis*-$[W(N_2)_2(PMe_2Ph)_4]^+$ and *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$ are 79 (10) and 228 (35), and 89 (4) and 246 (13), respectively. The large positive entropy of activation change for the step involving N_2 loss from *cis*- and *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$, which is significantly greater than the corresponding values obtained for neutral bis(dinitrogen) complexes, suggests a productlike transition state with extensive W–N_2 bond weakening.

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Registry No. *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, 28915-53-9; *trans*-$[W(N_2)_2(PMe_2Ph)_4]$, 139405-90-6; $[WCl_4(PMe_2Ph)_2]$, 30411-60-0; WCl_6, 13283-01-7; *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$, 139348-54-2; *cis*-$[W(N_2)_2(PMe_2Ph)_4]^+$, 139405-91-7.

(20) The rate constants (k_1) were determined using the following expression: $n_{app} = 2 - \exp(-k_1 t)$ (see ref 21).
(21) See for example: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 11.

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Coordination Polymers of Tetracyanoethylene with Metal Hexafluoroacetylacetonates: Formation and X-ray Crystal Structures

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Introduction

Tetracyanoethylene has been observed to react with metal complexes to form charge-transfer adducts,[1,2] alkene carbon bonded complexes,[3,4] and nitrile nitrogen donor complexes.[5,6] Neutral and reduced forms of TCNE ($TCNE^-$, $TCNE^{2-}$) can also potentially use nitrile coordination to bridge metal centers in forming coordination polymers. $[Co(acacen)_2{\cdot}TCNE]_x$[5a] and $[Sn(acac)_2{\cdot}TCNE]_x$[5b] are possible examples for this general type of coordination polymer, but structural characterization is lacking. This paper reports the formation and X-ray structure determinations for metal hexafluoroacetylacetonate complexes of TCNE, $[M(hfacac)_2{\cdot}TCNE]_x$, which occur as linear-chain coordination

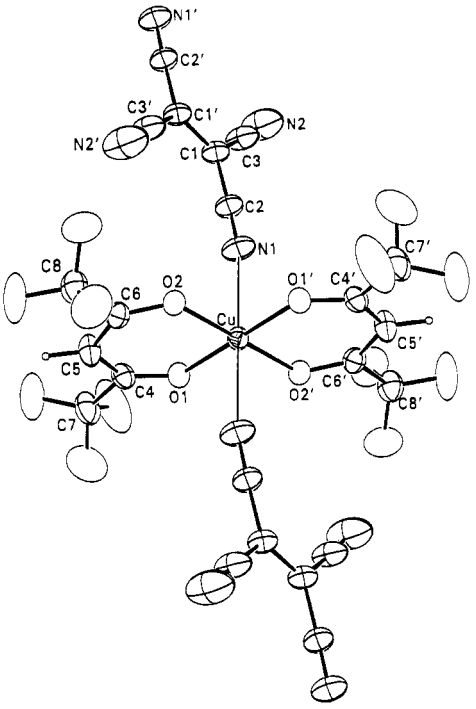

Figure 1. ORTEP view of the unit molecular structure of the coordination polymer $[Cu(hfacac)_2{\cdot}TCNE]_x$ showing the atom numbering and thermal motion ellipsoids (30%) for the non-hydrogen atoms. The molecular structure of $[Co(hfacac)_2{\cdot}TCNE]_x$ is essentially identical except for the M–NC axial ligand distance. The Cu–NC distance (2.563 Å) is significantly longer than the Co–NC distance (2.209 Å).

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