Journal of Organometallic Chemistry, 263 (1984) 359–369
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

OXIDATIVE-ADDITION REACTIONS OF $M(CO)_4(N–N)$ (M = Mo or W) USING IODOBENZENE DICHLORIDE. ISOLATION OF SEVEN-COORDINATE CATIONS OF MOLYBDENUM(II) AND TUNGSTEN(II) CONTAINING ALKYL ISOCYANIDE AND BIDENTATE N-HETEROCYCLE LIGANDS

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(Received July 1st, 1983)

Summary

A series of seven-coordinate tungsten(II) salts $[W(CNR)_5(N–N)](PF_6)_2$ (R = $CHMe_2$, CMe_3, C_6H_{11}, or CH_2Ph; N–N = bipy, Me_2bipy, or phen) have been prepared in high yield (> 75%). The synthetic procedure involves the oxidation of the metal carbonyl derivative $W(CO)_4(N–N)$ with iodobenzene dichloride, followed by displacement of carbon monoxide and chloride ligands from the intermediate $W(CO)_3(N–N)Cl_2$ by alkyl isocyanide. These reactions work equally well for the conversion of $Mo(CO)_4(N–N)$ to $[Mo(CNR)_5(N–N)](PF_6)_2$. The dealkylation of $[W(CNCMe_3)_5(N–N)](PF_6)_2$ to give $[\{W(CNCMe_3)_4(N–N)\}_2(\mu\text{-}CN)](PF_6)_3$ occurs in refluxing ethanol. The direct reaction of $[W(CNCMe_3)_7](PF_6)_2$ with N–N in refluxing 1-propanol leads to the dealkylation product $[W(CNCMe_3)_6(CN)]PF_6$, but there is no evidence for the substitution of the Me_3CNC ligands by N–N via such a route.

Introduction

A previous study [1] of seven-coordinate mixed alkyl isocyanide-nitrogen donor ligand compounds of molybdenum(II) led to the discovery of a series of complexes possessing the stoichiometries $[Mo(CNR)_5(N–N)](PF_6)_2$ (R = CH_3, $CHMe_2$, CMe_3, or C_6H_{11}), $[Mo(CNR)_6py](PF_6)_2$ (R = CMe_3 or C_6H_{11}), and $[\{Mo(CNCMe_3)_4(N–N)\}_2(\mu\text{-}CN)](PF_6)_3$ (N–N = bipy, Me_2bipy, or phen). In order to explore the generality of the dealkylation of coordinated t-butyl isocyanide in seven-coordinate metal(II) species, with a view to generating other cyano-bridged complexes, we focused our attention on the reactions of the tungsten(II) homoleptic alkyl isocyanide complexes $[W(CNR)_7](PF_6)_2$ with heterocyclic tertiary amines.

In contrast to the behaviour of the related molybdenum(II) systems, the com-

0022-328X/84/$03.00

plexes $[W(CNR)_7](PF_6)_2$ failed to react with N–N (bipy, Me_2bipy, and phen) within reasonable periods of time. Accordingly, we sought alternative means of preparing the tungsten(II) species $[W(CNR)_5(N-N)]^{2+}$. We now report a high yield procedure for the synthesis of the salts $[W(CNR)_5(N-N)](PF_6)_2$ through the oxidative-addition reactions of $W(CO)_4(N-N)$ (N–N = bipy, Me_2bipy, and phen) with $PhICl_2$ in the presence of RNC. This procedure can also be used to convert $Mo(CO)_4(N-N)$ to $[Mo(CNR)_5(N-N)](PF_6)_2$. The compounds $[W(CNCMe_3)_5(N-N)](PF_6)_2$ are convenient precursors to the cyano-bridged ditungsten(II) complexes $[\{W(CNCMe_3)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$.

Experimental

Starting materials

The following compounds were prepared by standard literature procedures: isopropyl isocyanide [2], t-butyl isocyanide [2], cyclohexyl isocyanide [2], benzyl isocyanide [2], iodobenzene dichloride ($PhICl_2$) [3], $M(CO)_4(N-N)$ [4] (M = Mo and W; N–N = bipy and phen), and $[W(CNR)_7](PF_6)_2$ [5] (R = CMe_3 and C_6H_{11}). $M(CO)_4(Me_2bipy)$ (M = Mo and W) was prepared by treating $M(CO)_6$ and Me_2bipy in toluene (where M = Mo) or xylene (where M = W) at reflux for 2 h. The work-up procedure was then identical to that described by Stiddard [4]. The compounds 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy), 1,10-phenanthroline (phen), $Mo(CO)_6$, and $W(CO)_6$ were obtained from commercial sources, as were all other reagents and solvents, and were used as received.

Reaction procedures

All reactions were carried out in an atmosphere of N_2 and all solvents were dried over molecular sieves and deoxygenated by purging with N_2 gas prior to use. In general, an excess of KPF_6 was added to those reaction mixtures where the reacting species started as their PF_6^- salts; this prevented the formation of products containing the $[HPO_4]^{2-}$ counter anion [5]. In those cases where complexes were prepared by very similar procedures (see Sections A–E), details of representative recipes only will be given.

A. Reactions of $[W(CNCMe_3)_7](PF_6)_2$ with bipy and phen

$[W(CNCMe_3)_6(CN)]PF_6$. Typically, a mixture of $[W(CNCMe_3)_7](PF_6)_2$ (0.5 g, 0.474 mmol), bipy (0.5 g, 3.20 mmol), and KPF_6 (0.5 g, 2.72 mmol) in 15 ml of deoxygenated 1-propanol was refluxed for 16 h. The reaction solution was cooled to 0°C, filtered, and the brown filtrate blown to dryness under a stream of nitrogen gas. The dark green-brown solid was recrystallized from a dichloromethane/diethyl ether mixture (2/1), and the resulting yellow powder washed with water and diethyl ether, and dried in vacuo; yield 0.24 g (60%). Anal. Found: C, 43.79; H, 6.79. $C_{31}H_{54}F_6N_7PW$ calcd.: C, 43.62; H, 6.33%.

This same yellow complex was obtained from the reaction between $[W(CNCMe_3)_7](PF_6)_2$ (0.5 g, 0.474 mmol) and phen (0.5 g, 2.78 mmol) in 20 ml of 1-propanol yield 0.26 g (64%). This product was shown by cyclic voltammetry and its spectroscopic properties to be identical with the sample of $[W(CNCMe_3)_6(CN)]PF_6$ as prepared above.

B. Reaction of $[W(CNC_6H_{11})_7](PF_6)_2$ *with bipy*

The reaction between $[W(CNC_6H_{11})_7](PF_6)_2$ (0.5 g, 0.402 mmol), bipy (0.5 g, 3.20 mmol), and KPF_6 (0.5 g, 2.72 mmol) in refluxing 1-propanol (20 ml) was carried out for 24 h. The resulting yellow-green solution was cooled to 0°C, filtered, and the filtrate blown to dryness under a stream of nitrogen gas. The yellow powder that was obtained after recrystallization from acetone/diethyl ether, was shown by cyclic voltammetry and its spectroscopic properties to be unreacted starting material $[W(CNC_6H_{11})_7](PF_6)_2$.

C. Oxidative-addition reactions of $M(CO)_4(N\text{-}N)$ *(M = Mo or W; N–N = bipy,* Me_2*bipy, or phen) with* $PhICl_2$*. Synthesis of seven-coordinate cations of molybdenum(II) and tungsten(II) of the type* $[M(CNR)_5(N\text{-}N)](PF_6)_2$

$[Mo(CNCMe_3)_5(bipy)](PF_6)_2$. Typically, a saturated solution of $Mo(CO)_4$(bipy) (1.71 g, 4.70 mmol) in 125 ml of deoxygenated methanol was stirred for 15 min at room temperature in a three-necked flask (which had been sheathed in aluminum foil to exclude light from the reaction mixture). Addition of solid $PhICl_2$ (1.94 g, 7.06 mmol) to the orange solution resulted in CO gas evolution. The reaction mixture was then stirred for a further 30 min at room temperature. A quantity of t-butyl isocyanide (4.0 ml, 0.0379 mol) was syringed into the pale yellow alcoholic solution thereby changing its color to a dark orange-red. The resulting reaction mixture was stirred at room temperature for an additional 16 h, and the dark red solution then filtered into a KPF_6/acetone solution (2 g of KPF_6 in 15 ml of acetone). The volume of the methanol solution was reduced under a stream of nitrogen gas, and the dark red-orange crystalline product that precipitated was collected by filtration and washed with water, diethyl ether, and methanol. The product was recrystallised from a methanol/diethyl ether mixture (2/1); yield 3.37 g (76%). Analytical data for this and similarly prepared cationic compounds are given in Table 1.

D. Formation of the cyano-bridged complexes $[\{W(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ *(N–N = bipy,* Me_2*bipy, and phen), via dealkylation of a t-butyl isocyanide ligand in* $[W(CNCMe_3)_5(N\text{-}N)](PF_6)_2$

(i) $[\{W(CNCMe_3)_4(Me_2bipy)\}_2(\mu\text{-}CN)](PF_6)_3$. A mixture of $[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$ (0.5 g, 0.466 mmol) and KPF_6 (0.5 g, 2.72 mmol) in 60 ml of ethanol was heated at reflux for 36 h. The reaction mixture was stirred at a very fast rate to ensure that the partially soluble starting material would not decompose thermally due to hot spots on the surface of the flask. Upon completion of the reflux, the dark purple-blue reaction mixture was cooled to 0°C, filtered, and the dark red crystalline product washed with copious amounts of water, diethyl ether, and petroleum ether before drying in vacuo. The dark red product, $[\{W(CNCMe_3)_4(Me_2bipy)\}_2(\mu\text{-}CN)](PF_6)_3$, was recrystallized from dichloromethane/diethyl ether, and acetone/diethyl ether, yield 0.32 g (62%). Anal. Found: C, 41.70; H, 5.43. $C_{65}H_{96}F_{18}N_{13}P_3W_2$ calcd.: C, 41.92; H, 5.16%.

The dark purple-blue filtrate that remained after harvesting the cyano-bridged species was evaporated to dryness under a stream of nitrogen gas. The oily residue was examined by IR and ^1H NMR spectroscopies and cyclic voltammetry, and was shown to be composed of a mixture of the starting material $[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$, and what we suspect to be $[W(CNCMe_3)_4(Me_2bipy)(CN)]PF_6$

($E_{1/2}$ at +0.41 V vs. SCE). No attempt was made to separate the components of this mixture.

(ii) $[\{W(CNCMe_3)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$. Yield 65%. Anal. Found: C, 40.42; H, 5.06. $C_{61}H_{88}F_{18}N_{13}P_3W_2$ calcd.: C, 40.56; H, 4.88%.

(iii) $[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$. Yield 58%. Anal. Found: C, 42.84; H, 5.14; N, 9.70. $C_{65}H_{88}F_{18}N_{13}P_3W_2$ calcd.: C, 42.10; H, 4.75; N, 9.82%.

E. Attempted preparation of the complexes $[\{M(CNCH_2Ph)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$ *(M = Mo and W) via dealkylation of a coordinated benzyl isocyanide ligand in* $[M(CNCH_2Ph)_5(bipy)](PF_6)_2$

Quantities of $[M(CNCH_2Ph)_5(bipy)](PF_6)_2$ (M = Mo and W) and KPF_6 were heated at reflux in a variety of solvents (e.g. methanol, ethanol, 1-propanol, and acetonitrile) for periods of up to 3 days. In all cases, the material retrieved from the reaction solutions was identified as starting material by cyclic voltammetry and ^1H NMR spectroscopy.

Physical measurements

IR spectra of Nujol mulls were recorded in the 4800–400 cm^{-1} region between KBr plates on an IBM Instruments Inc. IR/32 Fourier transform spectrometer. Nuclear magnetic resonance spectra were recorded using a Perkin–Elmer R-32 90MHz spectrometer. Resonances were referenced internally, usually to the residual

TABLE 1

YIELDS AND ANALYTICAL DATA FOR THE SEVEN-COORDINATE CATIONIC COMPOUNDS OF MOLYBDENUM(II) AND TUNGSTEN(II)

Compound	Molecular formula	Yield (%)	Analysis (Found (calcd.) (%))		
			C	H	N
$[Mo(CNCMe_3)_5(bipy)](PF_6)_2$	$C_{35}H_{53}F_{12}MoN_7P_2$	76	44.22 (43.89)	5.75 (5.58)	
$[Mo(CNCH_2Ph)_5(bipy)](PF_6)_2$	$C_{50}H_{43}F_{12}MoN_7P_2$	83	53.23 (53.24)	3.82 (3.82)	
$[Mo(CNCMe_3)_5(phen)](PF_6)_2$	$C_{37}H_{53}F_{12}MoN_7P_2$	78	45.30 (45.26)	5.48 (5.40)	9.80 (9.90)
$[W(CNCHMe_2)_5(bipy)](PF_6)_2$	$C_{30}H_{43}F_{12}N_7P_2W$	75	36.97 (36.93)	4.33 (4.41)	
$[W(CNCMe_3)_5(bipy)](PF_6)_2$	$C_{35}H_{53}F_{12}N_7P_2W$	76	40.02 (40.20)	5.35 (5.07)	
$[W(CNC_6H_{11})_5(bipy)](PF_6)_2$	$C_{45}H_{63}F_{12}N_7P_2W$	77	45.99 (45.96)	5.74 (5.36)	
$[W(CNCH_2Ph)_5(bipy)](PF_6)_2$	$C_{50}H_{43}F_{12}N_7P_2W$	85	49.35 (49.39)	3.62 (3.54)	7.99 (8.07)
$[W(CNCHMe_2)_5(Me_2bipy)](PF_6)_2$	$C_{32}H_{47}F_{12}N_7P_2W$	80	38.82 (38.29)	4.59 (4.69)	
$[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$	$C_{37}H_{57}F_{12}N_7P_2W$	85	40.99 (41.39)	5.14 (5.31)	8.82 (9.13)
$[W(CNCHMe_2)_5(phen)](PF_6)_2$	$C_{32}H_{43}F_{12}N_7P_2W$	76	38.29 (38.44)	4.41 (4.31)	
$[W(CNCMe_3)_5(phen)](PF_6)_2$	$C_{37}H_{53}F_{12}N_7P_2W$	78	41.09 (41.54)	5.07 (4.96)	

protons in the incompletely deuterated solvents. Electronic absorption spectra were recorded on methanol solutions using a Varian Series 634 spectrophotometer.

Electrochemical measurements were made on dichloromethane solutions containing 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, taken as $(E_{p,a} + E_{p,c})/2$, were referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2°C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett–Packard Model 7015B x-y recorder. All voltammetric measurements were made at a platinum bead electrode in solutions deaerated in a stream of nitrogen.

Elemental analyses (Table 1) were performed by Dr. H.D. Lee of the Purdue University microanalytical laboratory.

Results and discussion

The reactions of the homoleptic molybdenum(II) species $[Mo(CNR)_7](PF_6)_2$ (for $R = CH_3$, $CHMe_2$, and C_6H_{11}) with bidentate N-heterocyclic ligands (N–N = bipy, Me_2bipy, or phen) produce intense red-purple colored seven-coordinate substitution products $[Mo(CNR)_5(N{-}N)](PF_6)_2$ in which two isocyanide ligands have been replaced [1]. However, in the case of the reaction between the t-butyl isocyanide derivative $[Mo(CNCMe_3)_7](PF_6)_2$ and N–N, the novel dimolybdenum(II) cyano-bridged complexes $[\{Mo(CNCMe_3)_4(N{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ are formed in a complex reaction in which direct substitution is accompanied by the dealkylation of a coordinated isocyanide ligand followed by the coupling of two molybdenum centers through a cyanide bridge [1].

Attempts to prepare the analogous tungsten(II) complexes $[W(CNR)_5(N{-}N)](PF_6)_2$ and $[\{W(CNR)_4(N{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ from the homoleptic species $[W(CNR)_7]^{2+}$ were thwarted by the kinetic stability of the latter. Thus, $[W(CNC_6H_{11})_7](PF_6)_2$ failed to react directly with bipy or phen while the corresponding reactions of $[W(CNCMe_3)_7(PF_6)_2$ in refluxing 1-propanol gave the stable dealkylation product $[W(CNCMe_3)_6(CN)]PF_6$; there was no evidence for substitution of RNC by N–N. A convenient method for synthesizing $[W(CNR)_5(N{-}N)](PF_6)_2$ (for $R = CHMe_2$, CMe_3, C_6H_{11}, and CH_2Ph) has now been devised and shown to be equally convenient for the synthesis of the molybdenum(II) complexes. It thus provides an alternative procedure for the preparation of the previously described complexes $[Mo(CNR)_5(N{-}N)](PF_6)_2$ [1].

Synthesis of seven-coordinate mixed bidentate nitrogen donor ligand-alkyl isocyanide complexes of molybdenum(II) and tungsten(II)

The compounds $M(CO)_4(N{-}N)$ (M = Mo and W; N–N = bipy and phen) are known to undergo oxidative-addition type reactions with Br_2, I_2, ICN, and pseudohalogens [4,6,7] which offer a convenient preparative route to diamagnetic seven-coordinate complexes. However, in many cases, the products may be light and air sensitive [4,6].

Recently, Lippard and co-workers [5] reported the synthesis of seven-coordinate molybdenum(II) and tungsten(II) isocyanide complexes through the action of mild oxidants such as $PhICl_2$ and I_2 on $M(CNR)_x(CO)_{6-x}$ ($x = 1$, 2, or 3; R = alkyl or aryl; M = Mo or W). The oxidation potentials of these mixed isocyanide-carbonyl

TABLE 2

SPECTROSCOPIC PROPERTIES OF MIXED NITROGEN DONOR LIGAND-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

Complex	IR absorptions (cm^{-1}) [a]		Electronic absorption spectra (nm) [c]
	ν(C≡N)	ν(C=N) [b]	
$[Mo(CNCMe_3)_5(bipy)](PF_6)_2$ [d]	2185(m),2150(sh),2113(vs),2052(sh)	1602(m)	512(4.8),310(7.0)
$[Mo(CNCH_2Ph)_5(bipy)](PF_6)_2$	2206(m),2170(vs),2129(vs)	1608(m)	505(4.2),330(sh)
$[Mo(CNCMe_3)_5(phen)](PF_6)_2$	2185(m),2145(sh),2114(vs),2060(sh)	1630(w),1603(w),1580(w)	516(4.6),393(2.4),325(sh)
$[W(CNCHMe_2)_5(bipy)](PF_6)_2$	2196(m),2151(vs),2113(vs),2037(m)	1606(m)	525(4.8),339(7.7)
$[W(CNCMe_3)_5(bipy)](PF_6)_2$	2181(m),2142(sh),2108(vs),2053(sh)	1605(m)	525(4.9),341(8.2)
$[W(CNC_6H_{11})_5(bipy)](PF_6)_2$	2204(m),2163(vs),2111(vs)	1603(m)	531(4.9),341(8.2)
$[W(CNCH_2Ph)_5(bipy)](PF_6)_2$	2200(m),2161(vs),2117(vs)	1610(m)	535(4.5),405(sh),339(8.4)
$[W(CNCHMe_2)_5(Me_2bipy)](PF_6)_2$	2198(m),2157(vs),2106(vs),2039(m)	1621(m)	511(4.6),338(8.8)
$[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$	2177(m),2140(sh),2111(vs),2048(m)	1619(m)	513(5.1),339(9.6)
$[W(CNCHMe_2)_5(phen)](PF_6)_2$	2210(m),2163(vs),2103(vs),2037(m)	1629(w),1601(w),1578(w)	520(4.5),410(3.6),320(sh)
$[W(CNCMe_3)_5(phen)](PF_6)_2$	2181(m),2139(sh),2104(vs),2059(sh)	1631(w),1602(w),1577(w)	525(5.0),408(3.9),325(sh)
$[\{W(CNCMe_3)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$	2151(s),2096(vs),2052(vs)	1606(m)	561(9.9),362(12.0)
$[\{W(CNCMe_3)_4(Me_2bipy)\}_2(\mu\text{-}CN)](PF_6)_3$	2151(s),2090(vs),2043(vs)	1620(m)	552(10.1),350(sh)
$[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$	2150(s),2125(s),2089(vs),2049(sh)	1631(w),1601(w),1580(w)	561(9.6),361(11.0)

[a] IR spectra recorded as Nujol mulls. [b] Vibrations associated with the bipy, Me_2bipy, or phen ligands. [c] Data recorded in methanol. ε_{max} values (M^{-1} cm^{-1} $\times 10^{-3}$) are given in parentheses [d] Data for this complex taken from ref. 1.

TABLE 3

^{1}H NMR CHEMICAL SHIFTS OF MIXED NITROGEN DONOR LIGAND-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

Complex	Chemical shifts, δ [a]	
	Alkyl	Aromatic
$[Mo(CNCMe_3)_5(bipy)](PF_6)_2$ [b]	1.53s	7.90td, 8.37td, 8.79d, 9.16d
$[Mo(CNCH_2Ph)(bipy)](PF_6)_2$	5.14s	7.35m, 7.63td, 8.26td, 8.61d, 9.03d
$[Mo(CNCMe_3)_5(phen)](PF_6)_2$	1.51s	8.30m, 8.43s, 9.02dd, 9.63dd
$[W(CNCHMe_2)_5(bipy)](PF_6)_2$	1.41d,4.55spt	7.88td, 8.35td, 8.79d, 9.27d
$[W(CNCMe_3)_5(bipy)](PF_6)_2$	1.57s	7.97td, 8.49td, 8.85d, 9.26d
$[W(CNC_6H_{11})_5(bipy)](PF_6)_2$	1.40br,1.80br,4.45br	7.89td, 8.39td, 8.85d, 9.35d
$[W(CNCH_2Ph)_5(bipy)](PF_6)_2$	5.26s	7.32m, 7.64td, 8.26td, 8.62d, 9.11d
$[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$	1.51s,2.67s	7.77d, 8.71s, 9.02d
$[W(CNCHMe_2)_5(Me_2bipy)](PF_6)_2$	1.40d,2.64s,4.55spt	7.68d, 8.64s, 9.03d
$[W(CNCHMe_2)_5(phen)](PF_6)_2$	1.37d,4.55spt	8.25m, 8.40s, 8.99dd, 9.69dd
$[W(CNCMe_3)_5(phen)](PF_6)_2$	1.48s	8.30m, 8.42s, 9.01dd, 9.68dd
$[\{W(CNCMe_3)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$ [c]	1.45s	7.66m, 8.22m, 8.58d, 8.70d
$[\{W(CNCMe_3)_4(Me_2bipy)\}_2(\mu\text{-}CN)](PF_6)_3$ [c]	1.42s,2.68s	7.37d, 7.95s, 8.03s, 8.28d, 8.43d
$[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$ [c]	1.40s, 1.37s	7.56m, 8.04s, 8.15s, 8.51m, 8.71d

[a] All spectra were recorded in acetone-d_6 unless stated otherwise (see footnote *c*). Abbreviations are as follows: br, broad; d, doublet; dd, doublet of doublets; m, multiplet; s, singlet; spt, septet; t, triplet; td, triplet of doublets. [b] Data for this complex taken from ref. 1. [c] Recorded in acetonitrile-d_3.

compounds decrease with increasing isocyanide substitution [8]. Likewise, the substitution of CO by N–N (bipy and phen), as in the conversion of $M(CO)_6$ to derivatives of the type $M(CO)_4(N\text{–}N)$ (M = Cr, Mo, and W) [9], leads to products that possess a more accessible oxidation. In accord with this, we find that methanol solutions of $M(CO)_4(N\text{–}N)$ can be oxidized by $PhICl_2$. In the absence of any added isocyanide ligand, the complexes $M(CO)_3(N\text{–}N)Cl_2$ (M = Mo or W; N–N = bipy, Me_2bipy, or phen) appear to be the principal reaction products; during the reactions these sparingly soluble and rather unstable complexes precipitate from solution. In one case, that of the oxidation of $W(CO)_4(bipy)$, the product was identified as $W(CO)_3(bipy)Cl_2$ on the basis of its IR spectrum [10]. This compound was quite unstable in the presence of both light and air (the molybdenum analogues were even more unstable) and so was only characterized by IR spectroscopy. The addition of the appropriate amount of alkyl isocyanide leads to the loss of the carbon monoxide and chloride ligands from these intermediates and the formation, in high yield, of the seven-coordinate complexes $[M(CNR)_5(N\text{–}N)](PF_6)_2$ (M = Mo or W; R = $CHMe_2$, CMe_3, C_6H_{11}, or CH_2Ph; N–N = bipy, Me_2bipy, or phen). The complexes prepared by this procedure are listed in Table 2 along with certain of their IR and electronic absorption spectral properties. Of the three molybdenum(II) complexes listed, only $[Mo(CNCMe_3)_5(bipy)](PF_6)_2$ has been prepared previously [1] and then by a different procedure. The spectral properties of the new complexes $[Mo(CNCH_2Ph)_5(bipy)](PF_6)_2$ and $[Mo(CNCMe_3)_5(phen)](PF_6)_2$ are in excellent agreement with those of other compounds of the type $[Mo(CNR)_5(N\text{–}N)](PF_6)_2$ [1]. In all cases the most noticeable feature is the occurrence of an intense $M(d) \rightarrow N\text{–}N(\pi^\star)$ electronic transition at ca. 520 nm [1], the existence of which explains the dark red-purple colors in these complexes. The ^{1}H NMR spectra of the complexes

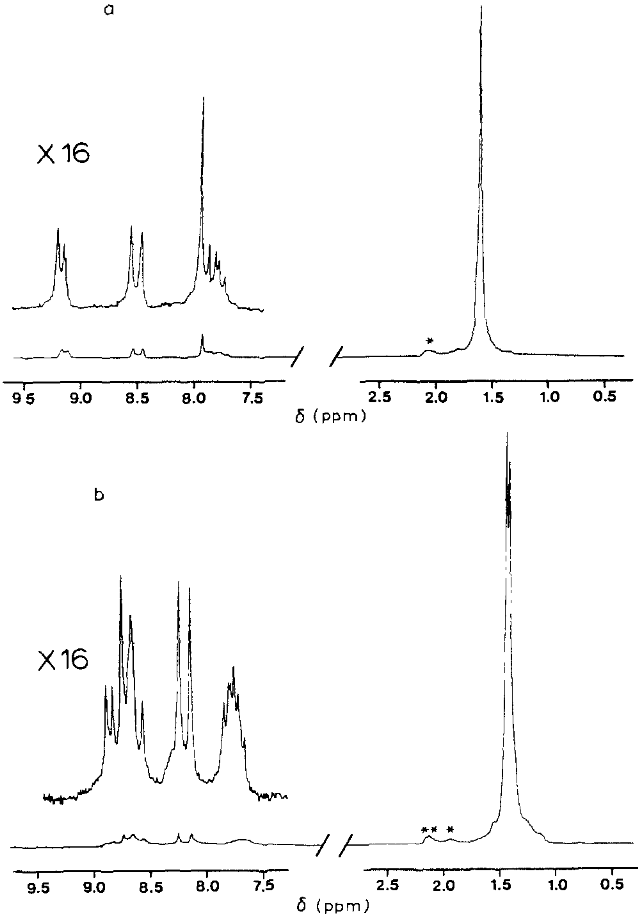

Fig. 1. The 90 MHz ^1H NMR spectrum of (a) $[W(CNCMe_3)_5(phen)](PF_6)_2$ (* denotes residual protons in acetone-d_6 and (b) $[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$ (* denotes residual protons in CD_3CN; ** denotes resonance due to H_2O in solvent) recorded at ambient temperature. Note that in spectrum (b) the t-butyl resonance is split into a doublet. We attribute this splitting to the magnetic inequivalence of the sets of Me_3CNC ligands that are bound to the inequivalent tungsten atoms. In the case of the related bipy and Me_2bipy complexes such a splitting is not resolvable. This same behavior was observed in the case of the ^1H NMR of $[\{Mo(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$.

(Table 3) are typical of the normal chelating bipy, Me_2bipy, and phen ligands [1,11]. Integration of these resonances and those associated to the coordinated isocyanide ligands showed excellent agreement with the expected stoichiometric ratios of the ligands.

Dealkylation of the complexes $[W(CNCMe_3)_5(N\text{-}N)](PF_6)_2$. Generation of the cyano-bridged species $[\{W(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$

When the complexes $[W(CNCMe_3)_5(N\text{-}N)](PF_6)_2$ (N–N = bipy, Me_2bipy, and phen) are refluxed in ethanol for 36 h, they are converted into the cyano-bridged ditungsten(II) products $[\{W(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ in good yield. In contrast to the molybdenum(II) systems, we find that the only route to the tungsten(II) analogues is via the dealkylation of $[W(CNCMe_3)_5(N{-}N)](PF_6)_2$.

The IR and electronic absorption spectral properties of the three cyano-bridged tungsten(II) complexes are listed in Table 2. The C≡N stretching frequencies in their IR spectra are somewhat different from those of $[M(CNCMe_3)_5(N{-}N)](PF_6)_2$, but cannot be interpreted in terms of any obvious structural dissimilarities since it has not proven possible to separate the ν(C≡N) modes of the coordinated RNC ligands from that which characterizes the CN bridge. The rather intense $W(5d) \rightarrow N{-}N(\pi^*)$ electronic absorption band at ca. 560 nm ($\varepsilon_{max} \simeq 10000$) is indicative of the existence of a cyanide bridged species [1]. The ^{1}H NMR spectra of all three complexes (Table 3) are much more complicated than those of the compounds $[W(CNR)_5(N{-}N)](PF_6)_2$; a spectral comparison of $[W(CNCMe_3)_5(phen)](PF_6)_2$ and $[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$ is given in Fig. 1. The striking difference between the two groups of compounds suggests, as we have discussed previously in the case of the dimolybdenum(II) complexes [1], the presence of two inequivalent bidentate nitrogen donor ligands in an unsymmetrical binuclear complex. The ligand resonances of the ditungsten(II) species are shifted upfield relative to those observed in the ^{1}H NMR spectra of the related dimolybdenum(II) complexes. At the same time the same general spectral pattern is seen [1].

Electrochemical properties

The electrochemical properties of the alkyl isocyanide complexes $[W(CNR)_5(N{-}N)](PF_6)_2$ are in accord with those expected on the basis of existing data for $[M(CNR)_7](PF_6)_2$ and various mixed isocyanide-ligand complexes of molybdenum(II) and tungsten(II) [1,12–14]. The voltammetric half-wave potentials vs. SCE for 0.2 *M* TBAH/dichloromethane solutions, as measured by the cyclic voltammetric technique, are presented in Table 4. Each of the mononuclear species $[M(CNR)_5(N{-}N)](PF_6)_2$ exhibits a couple at ca. +0.9 V for M = Mo, and ca. +0.8

TABLE 4

VOLTAMMETRIC VALUES FOR MIXED NITROGEN DONOR LIGAND-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II) [a]

Complex	$E_{p,a}$	$E_{1/2}$(ox)	$E_{p,c}$
$[Mo(CNCMe_3)_5(bipy)](PF_6)_2$ [b]	+1.73	+0.90	−1.22
$[Mo(CNCH_2Ph)_5(bipy)](PF_6)_2$	+1.80	+0.97	−1.14
$[Mo(CNCMe_3)_5(phen)](PF_6)_2$	+1.74	+0.92	−1.20
$[W(CNCHMe_2)_5(bipy)](PF_6)_2$	+1.43	+0.78	−1.23
$[W(CNCMe_3)_5(bipy)](PF_6)_2$	+1.48	+0.79	−1.22
$[W(CNC_6H_{11})_5(bipy)](PF_6)_2$	+1.54	+0.79	−1.22
$[W(CNCH_2Ph)_5(bipy)](PF_6)_2$	+1.56	+0.86	−1.17
$[W(CNCHMe_2)_5(Me_2bipy)](PF_6)_2$	+1.36	+0.75	−1.31
$[W(CNCMe_3)_5(Me_2bipy)](PF_6)_2$	+1.43	+0.75	−1.33
$[W(CNCHMe_2)_5(phen)](PF_6)_2$	+1.42	+0.78	−1.22
$[W(CNCMe_3)_5(phen)](PF_6)_2$	+1.46	+0.81	−1.20
$[\{W(CNCMe_3)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$	+1.36	+0.76, +0.58	−1.30, −1.53
$[\{W(CNCMe_3)_4(Me_2bipy)\}_2(\mu\text{-}CN)](PF_6)_3$	+1.34	+0.74, +0.55	−1.36, −1.59
$[\{W(CNCMe_3)_4(phen)\}_2(\mu\text{-}CN)](PF_6)_3$	+1.33	+0.72, +0.55	−1.32, −1.52

[a] In volts vs. SCE with a Pt bead electrode and 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Data for this complex taken from ref. 1.

V for M = W, which corresponds, in each case, to a one-electron oxidation (as determined by coulometry). These couples are characterized by $i_{p,a}/i_{p,c} = 1$ and a constant $i_p/v^{1/2}$ ratio for sweep rates between 50 and 400 mV/s. The potential separation between the anodic and cathodic peaks, ΔE_p, was close to 75 mV for a sweep rate of 200 mV/s and increased slightly with increase in sweep rate. The observations are in accord with this being a quasi-reversible electron-transfer process. These complexes also show a second (irreversible) oxidation at potentials more positive than +1.4 V and an irreversible reduction with $E_{p,c}$ between −1.14 and −1.33 V (see Table 4). The latter reduction is followed, on the reverse sweep, by the appearance of product waves at ca. −0.9 and −0.15 V vs. SCE for the molybdenum(II) species, and at ca. −0.8 and 0.0 V vs. SCE for the tungsten(II) species.

In contrast to the above electrochemical behavior, the cyano-bridged ditungsten(II) complexes of t-butyl isocyanide have cyclic voltammograms which display two reversible oxidations in the vicinity of the single reversible oxidation of $[W(CNR)_5(N-N)](PF_6)_2$ (i.e. $E_{1/2}(ox) \simeq +0.75$ and +0.55 V), plus two irreversible reductions ($E_{p,c} \simeq -1.35$ and −1.55 V), and a single irreversible oxidation ($E_{p,a} \simeq +1.35$ V). These electrochemical properties are in excellent agreement with those that characterize the analogous dimolybdenum(II) species (Table 4 and ref. 1) and thereby support the structure we have assigned to these tungsten complexes.

Attempted generation of the complexes $[\{M(CNCH_2Ph)_4(bipy)\}_2(\mu\text{-}CN)](PF_6)_3$ *(M = Mo and W) via dealkylation of a coordinated benzyl isocyanide ligand*

The dealkylation of coordinated t-butyl isocyanide ligands to form coordinated terminally bound cyanide, in the case of the conversion of $[M(CNCMe_3)_7](PF_6)_2$ (M = Mo and W) to $[M(CNCMe_3)_6(CN)]PF_6$, and bridging cyanides, in the case of the conversion of $[M(CNCMe_3)_5(N-N)](PF_6)_2$ (M = Mo and W) to $[\{M(CNCMe_3)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$, led us to question whether other cationic isocyanide complexes might not exhibit the same type of reactivity. The thermal dealkylation of a coordinated benzyl isocyanide ligand was deemed possible since the benzyl group can (like t-butyl) form a carbonium ion. However, when the compounds $[M(CNCH_2Ph)_5(bipy)](PF_6)_2$ (M = Mo and W) were refluxed in a variety of solvents, dealkylation did not occur and there was no evidence for the generation of any cyanide-bridged species.

Acknowledgement

Support from the National Science Foundation (Grant No. CHE82-06117) is gratefully acknowledged.

References

1 A. Bell, S.J. Lippard, M. Roberts, R.A. Walton, Organometallics, 2 (1983) 1562.
2 W.D. Weber, G.W. Gokel, I.K. Ugi, Angew. Chem. Int. Ed. Engl., 11 (1972) 530.
3 H.J. Lucas, E.R. Kennedy, Organic Sytheses, Wiley; New York, 1955; Collect. Vol. 3, p. 482.
4 M.H.B. Stiddard, J. Chem. Soc., (1962) 4712.
5 C.M. Giandomenico, L.H. Hanau, S.J. Lippard, Organometallics, 1 (1982) 142.
6 G.R. Dobson, M.M. Memering J. Inorg. Nucl. Chem., 35 (1973) 665.
7 W.A.G. Graham, R. Kummer, Inorg. Chem., 7 (1968) 310.

8 J.A. Connor, E.M. Jones, G.K. McEwen, M.K. Lloyd, J.A. McCleverty, J. Chem. Soc., Dalton Trans., (1972) 1246.

9 M.K. Lloyd, J.A. McCleverty, D.G. Orchard, J.A. Connor, M.B. Hall, I.H. Hillier, E.M. Jones, G.K. McEwen, J. Chem. Soc., Dalton Trans., (1973) 1743.

10 The CO stretching frequencies for $W(CO)_3(bipy)I_2$ are located at 2023, 1952, and 1910 cm^{-1}, and for $W(CO)_3(bipy)Br_2$ they are at 2037, 1959, and 1908 cm^{-1} [4]. The product we believe is $W(CO)_3(bipy)Cl_2$ has ν(CO) at 2040, 1954, and 1900 cm^{-1}.

11 See for example, S. Kitagaira, M. Murakata, N. Miyaji, Inorg. Chem., 21 (1982) 3842.

12 T.E. Wood, J.C. Deaton, J. Corning, R.E. Wild, R.A. Walton, Inorg. Chem., 19 (1980) 2614.

13 W.S. Mialki, R.E. Wild, R.A. Walton, Inorg. Chem., 20 (1981) 1380.

14 C. Caravana, C.M. Giandomenico, S.J. Lippard, Inorg. Chem., 21 (1982) 1860.