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MIXED ALKYL ISOCYANIDE-1,4-DIAZA-1,3-BUTADIENE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

ANDREW BELL and RICHARD A. WALTON*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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Summary

The reactions of $M(CO)_4(R'\text{-DAB})$ (M = Mo or W; R'-DAB = R'-N=CHCH=NR' (R' = i-propyl, t-butyl, or cyclohexyl)) with $SnCl_4$ in dichloromethane solution result in the formation, in high yield, of the orange, diamagnetic, seven-coordinate oxidative-addition products $M(CO)_3(R'\text{-DAB})(SnCl_3)Cl$. The reactions of $Mo(CO)_3(R'\text{-DAB})(SnCl_3)Cl$ (R' = i-Pr or Cy) with an excess of alkyl isocyanide RNC (R = $CHMe_2$, CMe_3, or C_6H_{11}) in the presence of KPF_6 lead to the formation of $[Mo(CNR)_4(R'\text{-DAB})Cl]PF_6$ or $[Mo(CNR)_5(R'\text{-DAB})](PF_6)_2$ depending upon the reaction stoichiometry and reaction conditions. The monocationic chloro species are converted to $[Mo(CNR)_5(R'\text{-DAB})](PF_6)_2$ upon reflux with the stoichiometric amount of RNC. Under similar reactions conditions $M(CO)_3(t\text{-Bu-DAB})(SnCl_3)Cl$ (M = Mo or W) derivatives react with alkyl isocyanides with the reductive-elimination of the elements of $SnCl_4$ and the formation of octahedral $M(CO)_3(CNR)(t\text{-Bu-DAB})$. The dark red compounds $[Mo(CNCMe_3)_5(R'\text{-DAB})](PF_6)_2$ (R' = i-Pr or Cy) react readily with cyanide ions at ambient temperatures in methanol to yield $[Mo(CNCMe_3)_4(R'\text{-DAB})(CN)]PF_6$. Attempts to thermally dealkylate the parent complexes $[Mo(CNCMe_3)_5(R'\text{-DAB})](PF_6)_2$ (R' = i-Pr or Cy) to these same cyano species were unsuccessful.

Introduction

The chemistry of high-coordinate early transition metal isocyanide complexes has received considerable attention recently [1–3], with the dealkylation [1,3–6] and reductive coupling [7–9] reactions of the isocyanide ligands in these and other compounds being of special interest. Our previous studies [1,4] in this area have dealt primarily with the synthesis of seven-coordinate mixed alkyl isocyanide-heterocyclic amine compounds of molybdenum(II) and tungsten(II) having the general formulae $[M(CNR)_5(N\text{-}N)](PF_6)_2$ (M = Mo or W; R = CH_3, $CHMe_2$, CMe_3, C_6H_{11}, or CH_2Ph; N–N = bipy, Me_2bipy, or phen) and $[Mo(CNR)_6(py)](PF_6)_2$ (R = CMe_3

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or C_6H_{11}). The dealkylation of coordinated t-butyl isocyanide in these seven-coordinate metal(II) species to give the cyanide-bridged complexes of the stoichiometry $[\{M(CNCMe_3)_4(N-N)\}_2(\mu-CN)](PF_6)_3$ (M = Mo or W; N–N = bipy, Me_2bipy, or phen) is especially noteworthy [1,4].

One synthetic method for the preparation of the molybdenum(II) complexes of the type $[Mo(CNR)_5(N-N)](PF_6)_2$ involved the direct reaction of $[Mo(CNR)_7](PF_6)_2$ with N–N. While these reactions worked satisfactorily for N–N = bipy, Me_2bipy, and phen, virtually no reaction was observed when the bidentate 1,4-disubstituted diaza-1,3-butadiene ligands (R′-DAB) [10] were used. Since these particular ligands are closely related to the well known nitrogen heterocyclic ligands bipy, Me_2bipy, and phen in that they too possess the common α-diimine moiety, -N=CC=N-, and have similar donor properties [11], we tried to establish whether our failure to prepare the complexes $[M(CNR)_5(R'-DAB)](PF_6)_2$ was a reflection of their instability. We now report that this is not the case. We describe the synthesis of molybdenum(II) and tungsten(II) complexes $M(CO)_3(R'-DAB)(SnCl_3)Cl$ through the oxidative-addition reactions of $M(CO)_4(R'-DAB)$ (R′ = $CHMe_2$, CMe_3, or C_6H_{11}) with $SnCl_4$. These seven-coordinate diamagnetic complexes react with alkyl isocyanides (RNC) to form the mixed isocyanide-R′-DAB complexes $[Mo(CNR)_4(R'-DAB)Cl]PF_6$ and $[Mo(CNR)_5(R'-DAB)](PF_6)_2$ by ligand substitution, and $M(CO)_3(CNR)(R'-DAB)$ by reductive-elimination of $SnCl_4$. An account of the reaction chemistry, and the spectroscopic and electrochemical properties of these mixed ligand complexes is given.

Experimental

Starting materials. The following compounds were prepared by standard literature procedures: methyl isocyanide [12], isopropyl isocyanide [13], t-butyl isocyanide [13], cyclohexyl isocyanide [13], N,N′-diisopropylethylenediimine (isopropyl-DAB or i-Pr-DAB) [14], *N,N′*-di-t-butylethylenediimine (t-butyl-DAB or t-Bu-DAB) [14], *N,N′*-dicyclohexylethylenediimine (cyclohexyl-DAB or Cy-DAB) [14,15], $Mo(CO)_4(R'-DAB)$ (R′ = i-Pr, t-Bu, or Cy) [16], and $Mo(CO)_3(Cy-DAB)(HgCl)Cl$ [17]. The complex $W(CO)_4(t-Bu-DAB)$ was prepared by heating a mixture of $W(CO)_6$ and t-butyl-DAB in xylene under reflux for 24 h. The work up was then identical to that described by tom Dieck [16]. 2,2′-Bipyridine (bipy), $SnCl_4$, 1.0 *M* $SnCl_4$ in dichloromethane, $HgCl_2$, $Mo(CO)_6$, $W(CO)_6$ and all other reagents and solvents were obtained from commercial sources, and were used as received.

Reaction procedures. All reactions were carried out under dry nitrogen atmosphere, and all solvents were deoxygenated prior to use by purging with N_2 gas. In general, an excess of KPF_6 was added to reaction mixtures in order to form species as their PF_6^- salts and to prevent the formation of products containing the $[HPO_4]^{2-}$ counter anion [5]. In those cases where complexes were prepared by similar procedures (see Sections A–H), only details of representative recipes will be given.

A. Reactions of $Mo(CO)_4(R'-DAB)$ (R′ = i-Pr, t-Bu, or Cy) with $SnCl_4$.

(i) $Mo(CO)_3(i-Pr-DAB)(SnCl_3)Cl$. A quantity of $Mo(CO)_4$(i-Pr-DAB) (0.5 g, 1.437 mmol) was stirred in 15 ml of dry dichloromethane at room temperature. The addition of $SnCl_4$ (0.17 ml, 1.445 mmol) dropwise into this dark red solution

resulted in immediate CO gas evolution, and the precipitation of an orange crystalline material. The reaction mixture was stirred for 3 h at room temperature, the pale orange solution was cooled to −10°C, and the bright orange crystals which had formed were filtered off, washed with diethyl ether followed by petroleum ether, and dried in vacuo; yield 0.83 g (84%). This complex, like the other $SnCl_4$ derivatives, could be recrystallized from acetone-diethyl ether or acetone/petroleum ether mixtures, if necessary. Anal.: Found: C, 23.03; H, 2.91; Cl, 23.83. $C_{11}H_{16}Cl_4MoN_2O_3Sn$ calcd.: C, 22.74; H, 2.76; Cl, 24.43%.

(ii) $Mo(CO)_3(t\text{-}Bu\text{-}DAB)(SnCl_3)Cl$. Yield 90%. Anal.: Found: C, 26.02; H, 3.39. $C_{13}H_{20}Cl_4MoN_2O_3Sn$ calcd.: C, 25.64; H, 3.29%.

(iii) $Mo(CO)_3(Cy\text{-}DAB)(SnCl_3)Cl$. Yield 78%. Anal.: Found: C, 31.12; H, 3.73. $C_{17}H_{24}Cl_4MoN_2O_3Sn$ calcd.: C, 30.89; H, 3.63%.

B. The reaction of $W(CO)_4(t\text{-}Bu\text{-}DAB)$ with $SnCl_4$. $W(CO)_3(t\text{-}Bu\text{-}DAB)(SnCl_3)Cl$.

The reaction between $W(CO)_4$(t-Bu-DAB) (1.18 g, 2.54 mmol) and $SnCl_4$ (0.32 ml, 2.72 mmol) in dichloromethane (40 ml) was carried out for 12 h at room temperature. The resulting insoluble orange powder was filtered off, washed with diethyl ether, and dried in vacuo; yield 1.26 g (71%). Anal.: Found: C, 22.10; H, 2.84. $C_{13}H_{20}Cl_4N_2O_3SnW$ calcd.: C, 22.40; H, 2.87%.

C. Reactions of $Mo(CO)_3(R'\text{-}DAB)(SnCl_3)Cl$ (R' = i-Pr or Cy) with alkyl isocyanides RNC ($R = CHMe_2$ or CMe_3).

(i) $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$. A quantity of $Mo(CO)_3$(Cy-DAB)-($SnCl_3$)Cl (0.5 g, 0.757 mmol) was dissolved in 50 ml of acetone at room temperature. The addition of 5.25 equivalents of t-butyl isocyanide (0.42 ml, 3.98 mmol) to the reaction vessel resulted in the evolution of CO and a color change from orange to dark blue. After a reaction period of 12 h, the solution was filtered into a KPF_6-acetone solution (0.5 g, in 10 ml acetone). A small amount of light gray material remained on the filter. The filtrate was dried under reduced pressure to yield a purple powder. The crude product was dissolved in a minimum of dichloromethane and the solution filtered. Treatment of the filtrate with 50 ml of diethyl ether gave a dark red solid. Yield of 0.51g (87%). This product was recrystallized from a methanol/diethyl ether mixture (1/2) to give 0.30 g (48%) of dark red crystals. Anal.: Found: C, 49.30; H, 7.58; N, 9.95; Cl, 4.69. $C_{34}H_{60}ClF_6MoN_6P$ calcd.: C, 49.25; H, 7.24; N, 10.14; Cl, 4.28%.

(ii) $[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)Cl]PF_6$. Blue-red crystals; yield 75%. Anal.: Found: C, 45.21; H, 7.14. $C_{28}H_{52}ClF_6MoN_6P$ calcd.: C, 44.90; H, 6.95%.

(iii) $[Mo(CNCMe_3)_5(Cy\text{-}DAB)](PF_6)_2$. A mixture of $Mo(CO)_3$(Cy-DAB) ($SnCl_3$)Cl (1.0 g, 1.51 mmol) and KPF_6 (0.56 g, 3.02 mmol) in 60 ml of ethanol was stirred at room temperature for 20 min. The addition of 8.0 equivalents of t-butyl isocyanide (1.28 ml, 12.08 mmol) to the above suspension caused an immediate color change to dark purple-red with concomitant CO gas evolution. The reaction mixture was then stirred at room temperature for a further 16 h. After the solution was cooled to 0°C, the dark red crystalline product was collected on a filter and washed with copious amounts of anhydrous diethyl ether; yield 1.44 g (93%). Dichloromethane/diethyl ether or methanol/diethyl ether mixtures can be used for recrystallization. Anal.: Found: C, 45.70; H, 6.76. $C_{39}H_{69}F_{12}MoN_7P_2$ calcd.: C, 45.84; H, 6.95%.

(iv) $[Mo(CNCMe_3)_5(i\text{-}Pr\text{-}DAB)](PF_6)_2$. Dark red crystals; yield 84%. Anal.: Found: C, 41.90; H, 6.85; N, 10.19. $C_{33}H_{61}F_{12}MoN_7P_2$ calcd.: C, 42.09; H, 6.48; N, 10.42%.

(v) $[Mo(CNCHMe_2)_5(Cy\text{-}DAB)](PF_6)_2$. Copper colored plates; yield 85%. Anal.: Found: C, 43.21; H, 6.71; N, 10.23. $C_{34}H_{59}F_{12}MoN_7P_2$ calcd C, 42.91; H, 6.20; N, 10.31%.

D. The Reaction of $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$ with t-butyl isocyanide.

$[Mo(CNCMe_3)_5(Cy\text{-}DAB)](PF_6)_2$. A mixture of $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$ (0.5 g, 0.604 mmol) and KPF_6 (0.5 g, 2.72 mmol) in 40 ml of methanol was warmed until the solids dissolved. Following the dropwise addition of 1.25 equivalents of t-butyl isocyanide to the reaction vessel, the solution was heated with reflux for 4 h, then cooled to 0°C, and finally dried. The dark red solid was collected, washed with water and diethyl ether, and recrystallized from a dichloromethane/diethyl ether mixture (1/2); yield 0.43 g (70%). The spectroscopic and electrochemical properties of this product were identical with those of the samples prepared by using the procedure described in C (iii).

E. Reactions of $Mo(CO)_3(R'\text{-}DAB)(HgCl)Cl$ (R' = i-Pr, t-Bu, or Cy) with t-butyl isocyanide.

(i) $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$. A quantity of $Mo(CO)_3(Cy\text{-}DAB)(HgCl)Cl$ was prepared from a mixture of $Mo(CO)_4(Cy\text{-}DAB)$ (0.43 g, 1.01 mmol), and $HgCl_2$ (0.273 g, 1.01 mmol) in 30 ml of dichloromethane by using the procedure described in ref. [17]. Without isolating the oxidative-addition product, neat t-butyl isocyanide (0.85 ml, 8.05 mmol) was syringed into the dark red-orange solution thereby changing its color to a darker red and causing CO gas evolution to occur. The resulting reaction mixture was stirred at room temperature for an additional 16 h, and then filtered into a KPF_6/acetone solution (1.0 g in 10 ml of acetone). A small quantity of light gray material ($HgCl_2$) and elemental mercury remained on the glass sinter. The volume of the resulting filtrate was reduced under a stream of nitrogen gas, and the dark purple insoluble product, $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$, was collected by filtration. Recrystallization of the product from dichloromethane/diethyl ether and methanol/diethyl ether mixtures yielded 0.55 g (65%) of a dark red crystalline material. The product was found by IR and ^1H NMR spectroscopies, and by cyclic voltammetry, to be identical to an authentic sample of $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$ as obtained in C (i).

(ii) $[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)Cl]PF_6$. Dark red-purple crystals; yield 57%. This complex was shown by its spectroscopic and electrochemical properties to be identical with the samples of $[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)Cl]PF_6$ prepared as described in C (ii).

(iii) Attempted preparation of $[Mo(CNCMe_3)_5(t\text{-}Bu\text{-}DAB)](PF_6)_2$. The addition of t-butyl isocyanide (1.40 ml, 13.25 mmol) to a mixture of $Mo(CO)_4(t\text{-}Bu\text{-}DAB)$ (0.60 g, 1.60 mmol) and $HgCl_2$(0.868 g, 3.20 mmol), which had been stirred at ambient temperature for 6 h, resulted in a dark orange solution after a total reaction time of 24 h. Work-up of the reaction mixture yielded the starting material $Mo(CO)_4(t\text{-}Bu\text{-}DAB)$ (0.46 g) as the only identified compound.

F. Reactions of $M(CO)_3(t\text{-}Bu\text{-}DAB)(SnCl_3)Cl$ (M = Mo or W) with alkyl isocyanides RNC ($R = CH_3$, CMe_3, or C_6H_{11}).

(i) $Mo(CO)_3(CNCMe_3)(t\text{-}Bu\text{-}DAB)$. A quantity of t-butyl isocyanide (1.39 ml, 13.2 mmol) was syringed into a suspension of $Mo(CO)_3$(t-Bu-DAB)($SnCl_3$)Cl (1.0 g, 1.643 mmol) and KPF_6 (1.0 g, 4.54 mmol) in 40 ml of ethanol and the reaction mixture was stirred for 24 h at room temperature. The dark purple solution was then filtered, and the filtrate dried under a stream of gaseous nitrogen. The gray insoluble material obtained by filtration was discarded. The greenish-gray solid obtained by evaporation of the filtrate was redissolved in dichloromethane, filtered to remove unreacted KPF_6, and the royal blue filtrate was again dried. The blue-purple solid produced was washed with petroleum ether and dried in vacuo. The product was recrystallized from a diethyl ether/petroleum ether mixture (1/5) to yield dark blue-purple crystals of $Mo(CO)_3(CNCMe_3)$(t-Bu-DAB); yield 0.56 g (79%). Anal.: Found: C, 49.71; H, 7.02; N, 9.69. $C_{18}H_{29}MoN_3O_3$ calcd.: C, 50.12; H, 6.78; N, 9.75%.

(ii) $Mo(CO)_3(CNCH_3)(t\text{-}Bu\text{-}DAB)$. Dark blue-purple crystals; yield 56%. Anal.: Found: C, 47.13; H, 6.02. $C_{15}H_{23}MoN_3O_3$ calcd.: C, 46.28; H, 5.91%.

(iii) $Mo(CO)_3(CNC_6H_{11})(t\text{-}Bu\text{-}DAB)$. This dark purple complex was prepared by a procedure analogous to that described in F (i) but with acetone as a reaction solvent; yield 66%. The identity of this compound was confirmed on the basis of its spectroscopic and electrochemical properties.

(iv) $W(CO)_3(CNCMe_3)(t\text{-}Bu\text{-}DAB)$. Yield 52%. Anal.: Found: C, 41.45; H, 5.79. $C_{18}H_{29}N_3O_3W$ calcd.: C, 41.63; H, 5.59%.

G. Reactions of $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$ (R' = i-Pr or Cy) with NaCN.

(i) $[MoCNCMe_3)_4(Cy\text{-}DAB)(CN)]PF_6$. The reaction between $[Mo(CNCMe_3)_5$(Cy-DAB)]$(PF_6)_2$ (0.26 g, 0.255 mmol), NaCN (0.05 g, 1.02 mmol), and KPF_6 (0.1 g, 0.544 mmol) in 15 ml of methanol was carried out at room temperature for 3 h and the solution changed from dark red to a golden yellow. Evaporation of the reaction solution gave an orange solid which was washed with water and diethyl ether, and, subsequently, recrystallized from dichloromethane/diethyl ether to give a crop of gilt platelets; yield 0.12 g (58%). Found: C, 51.08; H, 7.97; N, 11.73. Anal.: $C_{35}H_{60}F_6MoN_7P$ calcd.: C, 51.29; H, 7.33; N, 11.97%.

(ii) $[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)(CN)]PF_6$. Yield 38%. This complex was characterized on the basis of its spectroscopic and electrochemical properties.

H. The attempted dealkylation of a coordinated t-butyl isocyanide ligand in the complexes $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$.

Mixtures of $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$ (R' = i-Pr or Cy) 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 these cases, $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$ failed to react to give the desired dealkylation products $[Mo(CNCMe_3)_4(R'\text{-}DAB)(CN)]PF_6$ or $[\{Mo(CNCMe_3)_4(R'\text{-}DAB)\}_2(\mu\text{-}CN)](PF_6)_3$. The only identifiable product was the bright yellow complex $[Mo(CNCMe_3)_7](PF_6)_2$ whose identity was confirmed by a comparison of its spectroscopic and electrochemical properties with those exhibited by an authentic sample of $[Mo(CNCMe_3)_7](PF_6)_2$ [5].

Physical measurements. IR spectra were recorded as Nujol mulls between KBr plates or as dichloromethane solutions using an IBM Instruments IR/32 Fourier Transform (4800–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on an IBM Instruments 9420 UV-Visible spectrophotometer. ^{1}H NMR spectra were recorded at 90 MHz on a Perkin–Elmer R-32 spectrometer. The residual protons of acetone-d_6 (δ 2.05 ppm vs. TMS) were used as reference. Electrochemical measurements were made in dichloromethane solvents that contained 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$ and are referenced to the Ag/AgCl electrode at room temperature. Voltammetric experiments were performed using a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard model 7035B x-y recorder.

Analytical procedures. Elemental microanalyses were performed by Dr. H.D. Lee of the Purdue University microanalytical laboratory.

Results and discussion

(a) Reactions of the compounds Mo(CO)$_4$(R′-DAB) (R′ = isopropyl (i-Pr), t-butyl (t-Bu), or cyclohexyl (Cy)) and W(CO)$_4$(t-Bu-DAB) with SnCl$_4$.

The tetracarbonyl complexes Mo(CO)$_4$(R′-DAB) and W(CO)$_4$(t-Bu-DAB) react under mild conditions with one equivalent of SnCl$_4$ to give the oxidative-addition products of composition M(CO)$_3$(R′-DAB)(SnCl$_3$)Cl along with the evolution of CO. These seven-coordinate, yellow-orange, diamagnetic complexes are quite stable both in the solid state and when dissolved in polar solvents, such as acetone or dichloromethane. Table 1 gives the values of the IR-active ν(CO) modes. The spectral properties of the new complexes are in excellent agreement with the data reported for comparable compounds of the types M(CO)$_3$(N–N)(HgX)X [17,18] and M(CO)$_3$(N–N)(R$_n$M′X$_{3-n}$)X [19,20] (M = Mo or W; M′ = Sn or Ge; R = alkyl or aryl; X = Cl, Br, or I; n = 0, 1, or 2). The voltammetric peak potentials vs. Ag/AgCl for 0.2 M TBAH/dichloromethane solutions of the complexes, as measured by the cyclic voltammetry technique, are presented in Table 1 along with the corresponding

TABLE 1

INFRARED SPECTRA AND ELECTROCHEMICAL DATA FOR TETRACARBONYLMETAL-1,4-DIAZA-1,3-BUTADIENE COMPLEXES AND THEIR OXIDATIVE-ADDITION PRODUCTS

Complex	ν(C≡O) ^{a} (cm^{-1})	$E_{p,a}$ ^{b}	$E_{1/2}$(ox) ^{b}	$E_{p,c}$ ^{b}
Mo(CO)$_4$(i-Pr-DAB) ^{c}	2012s, 1917s, 1906s, 1859s	+1.69	+0.69	−1.50
Mo(CO)$_3$(i-Pr-DAB)(SnCl$_3$)Cl	2027s, 1950s, 1918s	+1.76	–	−0.31
Mo(CO)$_4$(t-Bu-DAB) ^{c}	2024s, 1910s, 1870s, 1805s	+1.76	+0.70	−1.47
Mo(CO)$_3$(t-Bu-DAB)(SnCl$_3$)Cl	2031s, 1943s, 1908s	+1.71	–	−0.37
Mo(CO)$_4$(Cy-DAB) ^{c}	2024s, 1931s, 1887s, 1818s	+1.72	+0.67	−1.51
Mo(CO)$_3$(Cy-DAB)(SnCl$_3$)Cl	2032s, 1958s, 1925s	+1.70	–	−0.36
W(CO)$_4$(t-Bu-DAB) ^{c}	2015s, 1905s, 1870s, 1805s	+1.82	+0.70	−1.38
W(CO)$_3$(t-Bu-DAB)(SnCl$_3$)Cl	2022s, 1937s, 1904s	+1.66	–	−0.35

^{a} IR spectra recorded as Nujol mulls between KBr plates. ^{b} In volts vs. Ag/AgCl with a Pt-bead electrode and 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Recorded at a scan rate of 200 mV/s. ^{c} IR spectra of these complexes agree closely with data reported previously in ref. 24.

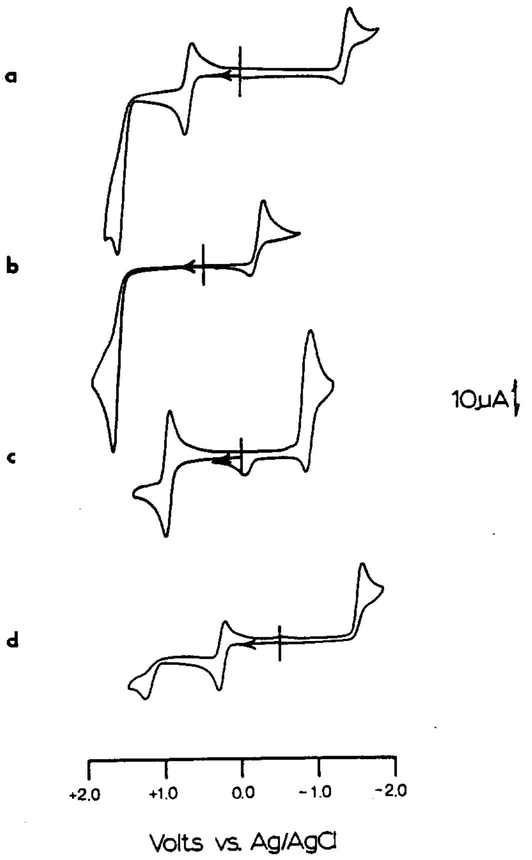

Fig. 1. Cyclic voltammograms in 0.2 *M* TBAH/dichloromethane solutions of (a) $Mo(CO)_4$(t-Bu-DAB), (b) $Mo(CO)_3$(i-Pr-DAB)($SnCl_3$)Cl, (c) $[Mo(CNCMe_3)_5$(Cy-DAB)]-$(PF_6)_2$, and (d) $Mo(CO)_3((CNCMe_3)$(t-Bu-DAB) recorded at 200 mV/s.

data for the starting complexes, $M(CO)_4$(R′-DAB), measured under these same conditions (see also Fig. 1).

The electrochemistry of the molybdenum and tungsten complexes $M(CO)_4$(R′-DAB) has been studied previously by tom Dieck [21] and our values are comparable to their data [22]. Each compound exhibits a reversible couple (in dichloromethane) at ca. +0.70 V, which corresponds, in each case, to a one-electron oxidation. These complexes further show a second (irreversible) oxidation at potentials greater than +1.4 V, and an irreversible ligand-based reduction with $E_{p,c}$ between −1.35 V and −1.55 V (see Table 1 and Fig. 1). In contrast, each of the mononuclear seven-coordinate species $M(CO)_3$(R′-DAB)($SnCl_3$)Cl exhibits an irreversible oxidation at ca. +1.7 V, and an irreversible reduction at ca. −0.3 V for M = Mo or W.

(b) Reactions of $M(CO)_3$(R′-DAB)($SnCl_3$)Cl (M = Mo or W) and $Mo(CO)_3$(R′-DAB)(HgCl)Cl with alkyl isocyanides

The reactions of dichloromethane or acetone solutions of the oxidative-addition products $Mo(CO)_3$(R′-DAB)($SnCl_3$)Cl and $Mo(CO)_3$(R′-DAB)(HgCl)Cl (R′ = i-Pr or Cy) with stoichiometric proportions (ca. 1/5) of t-butyl isocyanide in the presence of KPF_6 lead to the formation of the salts $[Mo(CNR)_4(R'\text{-}DAB)Cl]PF_6$. In the presence of an excess of RNC (ca. 8 equivalents), ethanolic solutions of $Mo(CO)_3(R'\text{-}DAB)(SnCl_3)Cl$ (R' = i-Pr or Cy) are converted to the dark red cationic species $[Mo(CNR)_5(R'\text{-}DAB)]^{2+}$ ($R = CHMe_2$ or CMe_3), so that $[Mo(CNR)_4(R'\text{-}DAB)Cl]PF_6$ can be viewed as an intermediate in the conversion of $Mo(CO)_3(R'\text{-}DAB)(SnCl_3)Cl$ to $[Mo(CNR)_5(R'\text{-}DAB)](PF_6)_2$. This has been confirmed by the conversion of $[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$ to $[Mo(CNCMe_3)_5\text{-}(Cy\text{-}DAB)](PF_6)_2$ in high yield upon its reaction with t-butyl isocyanide (ca. 1 equivalent) and KPF_6.

In contrast to this behavior, when R' = t-Bu the complexes $M(CO)_3(R'\text{-}DAB)\text{-}(SnCl_3)Cl$ (M = Mo or W) * react with the resulting reductive-elimination of the elements of $SnCl_4$ and the formation of $M(CO)_3(CNR)(R'\text{-}DAB)$ (vide infra).

The new compounds prepared by the above method are dark red to purple crystalline solids. They are air-stable in the solid state and moderately stable in solution. The complexes are listed in Table 2 along with certain of their IR and electronic absorption spectral properties. The five molybdenum(II) complexes of the types $[Mo(CNR)_4(R'\text{-}DAB)Cl]PF_6$ and $[Mo(CNR)_5(R'\text{-}DAB)](PF_6)_2$ have $\nu(CN)$ modes in their IR spectra that are in very close agreement with those which are exhibited by the analogous seven-coordinate cations containing alkyl isocyanide and bidentate heterocyclic amine ligands i.e., $[M(CNR)_4(N\text{-}N)Cl]^+$ and $[M(CNR)_5\text{-}(N\text{-}N)]^{2+}$ (M = Mo or W; N–N = bipy, Me_2bipy, or phen) [1,4,23]. In all cases, the occurrence of an intense $M(d) \rightarrow N\text{-}N(\pi^*)$ electronic transition between ca. 500 and 600 nm explains the dark red-purple colors of these complexes. The ^1H NMR spectra of the complexes ** are typical of the normal chelating 1,4-diaza-1,3-butadiene ligands [24(a),25]. Integration of these resonances and those associated with the coordinated isocyanide ligands, together with the elemental microanalyses, showed excellent agreement with the proposed stoichiometries of these complexes.

A noteworthy reaction of the complexes $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$ (R' = i-Pr or Cy) is their conversion to $[Mo(CNCMe_3)_4(R'\text{-}DAB)(CN)]PF_6$ upon treating them with methanol solutions of CN^-. The spectroscopic properties of these complexes are given in Table 2 and are very similar to comparable data for analogous compounds reported in the literature [1,5]. The dealkylation of coordinated t-butyl isocyanide ligands has been reported previously [1,3–6], and is most commonly encountered among cationic isocyanide complexes. One example of special note is that of the dealkylation of a t-butyl ligand in the substituted homoleptic complexes $[M(CNCMe_3)_5(N\text{-}N)](PF_6)_2$ (M = Mo or W; N–N = bipy, Me_2bipy, or phen) to give the bimetallic cyano-bridged compounds $[\{M(CNCMe_3)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$ [1,4]. In the case of $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$, however, we were unable to induce thermal dealkylation. In view of the relative ease of preparing $[Mo(CNCMe_3)_4(R'\text{-}DAB)(CN)]PF_6$ by the simple substitution route described above, we can only ascribe this failure to dealkylate to the greatly enhanced thermal stability of $[Mo(CNCMe_3)_5(R'\text{-}DAB)](PF_6)_2$ over that

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* We have been unable, as yet, to prepare the analogous compounds $M(CO)_3(t\text{-}Bu\text{-}DAB)(HgCl)Cl$, and so have not explored their reactions with RNC.

** A table of ^1H NMR spectral data is available on request from R.A.W.

of [Mo(CNCMe)$_5$(N–N)](PF$_6$)$_2$ (N–N = bipy, Me$_2$bipy, or phen). However, we do not at present see an obvious reason for this.

(c) *The formation of the tricarbonyl derivatives M(CO)$_3$(CNR)(t-Bu-DAB) (M = Mo or W).*

As was mentioned in the preceding section, we were unable to prepare the [M(CNR)$_5$(t-Bu-DAB)](PF$_6$)$_2$ complexes by the reaction of an excess of RNC with M(CO)$_3$(t-Bu-DAB)(SnCl$_3$)Cl. Instead, reductive-elimination of the elements of SnCl$_4$ occurred and the dark blue-purple mononuclear monoisocyanide complexes Mo(CO)$_3$(CNR)(t-Bu-DAB) (R = CH$_3$, CMe$_3$, or C$_6$H$_{11}$) and W(CO)$_3$(CNCMe$_3$)(t-Bu-DAB) resulted. The IR spectra of the complexes (Table 2) show a single CN stretching mode at ~ 2150 cm^{-1} and three intense carbonyl stretching absorptions both in the solid state and in solution. This implies that the three carbonyl groups are in a facial arrangement and that the solid state structure of the complexes is the same as that in solution. The salient features of the electronic spectra are also given in Table 2.

TABLE 2

SPECTROSCOPIC PROPERTIES OF MIXED 1,4-DIAZA-1,3-BUTADIENE-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Complex	IR absorptions (cm^{-1}) [a] ν(C≡N) and/or ν(C≡O)	Electronic absorption spectra (nm) [c]
[Mo(CNCHMe$_2$)$_5$(Cy-DAB)](PF$_6$)$_2$	2232m, 2213m, 2201s, 2163s, 2126s, 2029m 2213m, 2193m, 2149s, 2120sh [b]	554(5800), 440(8800)
[Mo(CNCMe$_3$)$_5$(i-Pr-DAB)](PF$_6$)$_2$	2193sh, 2166m, 2124s, 2052sh 2197w, 2161m, 2126s, 2046*w* [b]	550(8700), 431(3900), 254(sh)
[Mo(CNCMe$_3$)$_5$(Cy-DAB)](PF$_6$)$_2$	2203m, 2170s, 2128s, 2053sh 2199m, 2164s, 2124s, 2053w [b]	552(7900), 435(3000), 250(sh)
[Mo(CNCMe$_3$)$_4$(i-Pr-DAB)Cl]PF$_6$	2146sh, 2136s, 2109s, 2051sh	592(7500), 418(5000), 268(sh), 252(sh)
[Mo(CNCMe$_3$)$_4$(Cy-DAB)Cl]PF$_6$	2181s, 2143s, 2112s, 2053sh	596(8000), 409(5300), 274(sh), 249(sh)
[Mo(CNCMe$_3$)$_4$(i-Pr-DAB)(CN)]PF$_6$	2174s, 2130s, 2047sh 2184m, 2141s, 2049w [b]	560(sh), 415(13600), 308(sh), 252(sh)
[Mo(CNCMe$_3$)$_4$(Cy-DAB)(CN)]PF$_6$	2183m, 2139s, 2049sh 2182m, 2139s, 2051w [b]	557(1200), 426(14300), 297(11400), 258(sh)
Mo(CO)$_3$(CNCH$_3$)(t-Bu-DAB)	2168s, 1910s, 1819s, 1790s 2159s, 1923s, 1837s, 1825s [b]	575(7000), 354(2700), 305(sh), 262(20000)
Mo(CO)$_3$(CNCMe$_3$)(t-Bu-DAB)	2141s, 1921s, 1835s, 1798s 2132s, 1900s, 1813s, 1798s [b]	579(6900), 351(2600), 305(sh), 259(20000)
Mo(CO)$_3$(CNC$_6$H$_{11}$)(t-Bu-DAB)	2137s, 1900s, 1817s, 1794s, 2134s, 1921s, 1835s, 1798s [b]	580(9300), 351(3600), 305(sh), 261(27000)
W(CO)$_3$(CNCMe$_3$)(t-Bu-DAB)	2137s, 1892s, 1810s, 1792s 2134s, 1918s, 1815s, 1796s [b]	585(10800), 350(2500), 310(sh), 257(25000)

[a] IR spectra recorded as Nujol mulls unless otherwise stated. [b] IR spectra recorded on dichloromethane solutions. [c] Data recorded in dichloromethane; ϵ_{max} values (M^{-1} cm^{-1}) are given in parentheses.

TABLE 3

CYCLIC VOLTAMMETRIC DATA FOR MIXED 1,4-DIAZA-1,3-BUTADIENE-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM AND TUNGSTEN [a]

Complex	$E_{p,a}$	$E_{1/2}$(ox)	$E_{p,c}$
$[Mo(CNCHMe_2)_5(Cy\text{-}DAB)](PF_6)_2$	–	+0.95	−0.94
$[Mo(CNCMe_3)_5(i\text{-}Pr\text{-}DAB)](PF_6)_2$	–	+0.98	−0.97
$[Mo(CNCMe_3)_5(Cy\text{-}DAB)](PF_6)_2$	–	+0.95	−0.97
$[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)Cl]PF_6$	+1.57	+0.63	−1.23
$[Mo(CNCMe_3)_4(Cy\text{-}DAB)Cl]PF_6$	+1.54	+0.57	−1.36
$[Mo(CNCMe_3)_4(i\text{-}Pr\text{-}DAB)(CN)]PF_6$	+1.65	+0.71	−1.60
$[Mo(CNCMe_3)_4(Cy\text{-}DAB)(CN)PF_6$	+1.63	+0.72	−1.48
$Mo(CO)_3(CNCH_3)(t\text{-}Bu\text{-}DAB)$	+1.34	+0.31	−1.60
$Mo(CO)_3(CNCMe_3)(t\text{-}Bu\text{-}DAB)$	+1.37	+0.30	−1.63
$Mo(CO)_3(CNC_6H_{11})(t\text{-}Bu\text{-}DAB)$	+1.60	+0.34	−1.59
$W(CO)_3(CNCMe_3)(t\text{-}Bu\text{-}DAB)$	+1.37	+0.28	−1.57

[a] In volts vs. Ag/AgCl with a Pt bead electrode and 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Recorded at a scan rate of 200 mV/s.

(d) Electrochemical properties of the mixed isocyanide-R′-DAB complexes of molybdenum and tungsten.

The electrochemical properties of the alkyl isocyanide complexes $[Mo(CNR)_5(R'\text{-}DAB)](PF_6)_2$, $[Mo(CNCMe_3)_4(R'\text{-}DAB)Cl]PF_6$, $[Mo(CNCMe_3)_4(R'\text{-}DAB)(CN)]PF_6$, and $M(CO)_3(CNR)(R'\text{-}DAB)$ (M = Mo or W) are presented in Table 3 and are in accord with those expected on the basis of existing data for $[Mo(CNR)_7](PF_6)_2$ [26,27], $[Mo(CNR)_5(P\text{–}P)](PF_6)_2$ (P–P = $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2\text{-}CH_2PPh_2$) [28], $[Mo(CNR)_5(N\text{–}N)](PF_6)_2$ [1,4,23], $[Mo(CNR)_4(N\text{–}N)Cl]PF_6$ [1], and $M(CO)_4(R'\text{-}DAB)$ (M = Mo or W) [21]. The half-wave or peak potentials vs. Ag/AgCl for 0.2 *M* TBAH/dichloromethane solutions were measured by the cyclic voltammetric technique, and the cyclic voltammograms of $[Mo(CNCMe_3)_5(Cy\text{-}DAB)](PF_6)_2$ and $Mo(CO)_3(CNCMe_3)(t\text{-}Bu\text{-}DAB)$ are shown in Figure 1. Each complex of the type $[Mo(CNR)_5(R'\text{-}DAB)](PF_6)_2$ exhibits a couple at ca. +1.0 V, corresponding to a one-electron oxidation (as determined by coulometry). This is characterized by $i_{p,a}/i_{p,c} = 1$ and a constant $i_p/\nu^{1/2}$ 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. These observations are in accord with this being a quasi-reversible electron-transfer process. Additionally, these complexes show an irreversible reduction close to −1.0 V (Fig. 1). The half-wave potentials ($E_{1/2}$(ox)) for the chloride and cyanide complexes of the type $[Mo(CNCMe_3)_4(R'\text{-}DAB)X]PF_6$ (R′ = i-Pr or Cy; X = Cl or CN) become more negative in the sequence CN < Cl. A similar trend has been observed in the redox properties of the molybdenum(II) complexes $[Mo(CNR)_6X]^+$ (X = Cl, Br, I, or CN) [27].

The tricarbonyl complexes $M(CO)_3(CNR)(t\text{-}Bu\text{-}DAB)$ possess a reversible oxidation at ca. +0.30 V vs Ag/AgCl, and a second (irreversible) oxidation between +1.3 V and +1.6 V. An irreversible reduction at $E_{p,c} \sim -1.6$ V is also observed (see Fig. 1). The electrochemical properties of these complexes are consistent with the expectation that upon the replacement of a CO ligand by a less effective π-acceptor (i.e., RNC) the potential for the M^I/M^0 couple should shift to a lower value compared to the parent $M(CO)_4$(t-Bu-DAB) compounds. Indeed, the complexes $Mo(CO)_3$(CNR)(R′-DAB) are easily oxidized to the corresponding monocations by rather mild oxidizing agents e.g., $[Cp_2Fe]PF_6$. The chemistry of these 17-electron species is currently under investigation.

(e) Concluding remarks

The preparation of the seven-coordinate complexes $[M(CNR)_5(R'\text{-DAB})](PF_6)_2$ (M = Mo or W; R′ = i-Pr or Cy) has required a new two-step synthetic strategy that is somewhat different from that used in the preparation of the complexes $[M(CNR)_5(N{-}N)](PF_6)_2$ (N–N = bipy, Me_2bipy, or phen). An oxidative-addition reaction (using $SnCl_4$ or $HgCl_2$) is first utilized to convert $M(CO)_4$(R′-DAB) to $M(CO)_3(R'\text{-DAB})(SnCl_3)Cl$ or $M(CO)_3$(R′-DAB)(HgCl)Cl. This is followed by a non-redox substitution step using an excess of RNC to generate $[M(CNR)_5(R'\text{-DAB})]^{2+}$. However, this approach is apparently very sensitive to the nature of the R′-DAB ligand for, in the case of R′ = t-Bu, the reaction of $M(CO)_3(t\text{-Bu-DAB})(SnCl_3)Cl$ with RNC proceeds with the reductive-elimination of the elements of $SnCl_4$ and the formation of the zerovalent complexes $M(CO)_3$(CNR)(t-Bu-DAB). Since there appears to be no compelling steric reason for this difference in behavior, we presume that it reflects some subtle difference in electronic factors. If the t-Bu-DAB ligand is slightly more basic than the two other R′-DAB ligands that have been used, then this may be sufficient to favor reductive elimination rather than substitution, especially in the presence of RNC ligands that can be very effective in the stabilization of low oxidation states.

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