MIXED ISOCYANIDE-1,4-DIAZA-1,3-BUTADIENE COMPLEXES OF MOLYBDENUM AND TUNGSTEN-II.* SPECIES OF THE TYPE [M(CO)₃(CNR)(R'-DAB)]^{1+,0,1-}

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Abstract-The complexes $M(CO)_4(R'-DAB)$ (M = Mo)or W; R'-DAB =R'-N=CH=CH=N-R'; R' = i-Pr, t-Bu, Cy or p-tol) undergo substitution of a single CO ligand by isocyanide ligands RNC (R = Me, CHMe₂, CMe₃, C₆H₁₁ or xylyl), in refluxing toluene to give $fac-M(CO)_{3}(CNR)(R'-DAB)$. Synthesis of the latter complexes can also be achieved, at ambient temperature, through the use of the nitrile complexes, $Mo(CO)_3(NCMe)_3$ and $W(CO)_3(NCEt)_3$: the method involves substitution of the nitrile ligands first by R'-DAB, then by RNC. The intermediate compounds Mo(CO)₃(NCMe)(R'-DAB) and W(CO)₃(NCEt)(R'-DAB) have also been isolated and characterized. Oxidation of dark blue-purple $Mo(CO)_3(NCMe)(t-Bu-DAB)$ and $Mo(CO)_3(CNR)(t-Bu-DAB)(R = Me or$ CMe_3) with $[Cp_2Fe]PF_6$ in dichloromethane solution produces the paramagnetic (17electron), orange complexes $[Mo(CO)_3(NCMe)(t-Bu-DAB)]PF_6$ and $[Mo(CO)_3(CNR)(t-Bu-DAB)]PF_6$ Bu-DAB)]PF₆, respectively. The molybdenum cations, $[Mo(CO)_3(NCMe)(t-Bu-DAB)]PF_6$ and $[Mo(CO)_3(CNCMe_3)(t-Bu-DAB)]PF_6$, react with two and one equivalent of tert-butyl isocyanide, respectively, to yield dark red cis, trans-[Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB)]PF₆. Reduction of cis, trans- $[Mo(CO)_2(CNCMe_3)_2(t-Bu-DAB)]PF_6$ with cobaltocene in acetone yields the analogous dark blue zerovalent species cis, $trans-Mo(CO)_2(CNCMe_3)_2(t-Bu-DAB)$. The compounds $[Mo(CO)(CNR)_4(t-Bu-DAB)](PF_6)_2$ and $Mo(CO)_3(CNR)(t-Bu-DAB)$ are produced, via a disproportionation reaction, when solutions of the cations $[Mo(CO)_3(CNR)(t-Bu-DAB)]^+$ (R = Me or CMe₃) are reacted with ~ three equivalents of RNC. On the other hand, the reaction between tert-butyl isocyanide and $[Mo(CO)_3(CNCMe_3)(i-Pr-DAB)]^+$ gives seven-coordinate [Mo(CNCMe₃)₅(*i*-Pr-DAB] $(PF_6)_2$ and Mo(CO)₃(CNCMe₃)(*i*-Pr-DAB). The ligand-based reduction of the complexes $M(CO)_3(CNR)(R'-DAB)$ (M = Mo or W) is readily accessible in THF upon addition of one molar equivalent of THF-soluble LiEt₃BH to yield solutions that contain the radical anions $[M(CO)_3(CNR)(R'-DAB)]^{-1}$. The complexes synthesized in this work have been characterized on the basis of their spectroscopic and electrochemical properties, including ESR spectral studies on the paramagnetic 17- and 19-electron complexes.

We have shown¹ that the reactions of the molybdenum(II) complexes $Mo(CO)_3(R'-DAB)$ -(SnCl₃)Cl, where R'-DAB represents R'-N= CH-CH=N-R', with an excess of alkyl iso-cyanide (CNR) in the presence of KPF₆ lead to the seven-coordinate mixed isocyanide-R'-DAB species

 $[Mo(CNR)_4(R'-DAB)Cl]PF_6$

and

$[Mo(CNR)_5(R'-DAB)](PF_6)_2$

in the case of R' = i-Pr or Cy. However, when the *tert*-butyl-DAB (*t*-Bu-DAB) ligand is used, such reactions proceed with the reductive elimination of the elements of SnCl₄ and the formation of Mo(CO)₃(CNR)(*t*-Bu-DAB). A similar reaction was used¹ to give the analogous tungsten(0) complex W(CO)₃(CNR)(*t*-Bu-DAB) in the case of $R = CMe_3$. We have now developed some general procedures for the synthesis of a broad range of complexes of the

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type $M(CO)_3(CNR)(R'-DAB)$. In this report we give an account of these syntheses and a full characterization of these complexes, including an examination of their redox chemistry. The generation and isolation of the 17-, 18- and 19-electron species $[M(CO)_3(CNR)(R'-DAB)]^{1+,0,1-}$ are described.

EXPERIMENTAL

Starting materials

The following compounds were prepared by standard literature procedures: methyl isocyanide,² isopropyl isocyanide,³ tert-butyl isocyanide,³ isocyanide,3 N,N'-di-iso-propylcyclohexyl ethylenediimine [isopropyl-DAB (*i*-Pr-DAB)],⁴ (t-Bu-DAB),⁴ N,N'-di-tert-butylethylenediimine N, N'-dicyclohexylethylenediimine [cyclohexyl-DAB (Cy-DAB)]^{4,5} Mo(CO)₄(R'-DAB) (R' = i-Pr, t-Bu or Cy).⁶ The complex W(CO)₄(t-Bu-DAB) was prepared by heating a mixture of W(CO)₆ and t-Bu-DAB in xylene at reflux for 24 h. The work up was then identical to that described by tom Dieck.⁶ Lithium triethylborohydride [1.0 M LiEt₃BH in THF ("Super-Hydride"), Aldrich Chemical Co.], ferrocene, cobaltocene and 2,6-dimethylphenyl isocyanide (xylylNC, Fluka AG) were obtained from commercial sources as were all reagents and solvents. The solvents dichloromethane, acetonitrile and THF were distilled under N₂ from P_4O_{10} , CaH₂ and sodium benzophenone ketyl, respectively, before use.

The hexacarbonyls $Mo(CO)_6$ and $W(CO)_6$ were obtained from Pressure Chemical Co. and were converted into the nitrile derivatives $Mo(CO)_3(NCMe)_3$ and $W(CO)_3(NCEt)_3$ using established procedures.^{7,8} For convenience in handling, these nitrile complexes were usually generated *in situ* and then reacted further with RNC or R'-DAB ligands.

Samples of the oxidizing agent ferricinium hexafluorophosphate ($[Cp_2Fe]PF_6$) were prepared as described in the literature.⁹

Reaction procedures

All reactions were carried out under a dry nitrogen atmosphere, and all reaction solvents were dried and deoxygenated prior to use by purging with N_2 gas for 15 min. In those cases where compounds were prepared by very similar procedures (see Sections A– D) details of representative preparations only will be given. In those instances where microanalytical data are not given, identification of products is based upon their spectroscopic and electrochemical properties.

A. Preparation of Mo(CO)₃(NCMe)(R'-DAB) $(\mathbf{R}' = t$ -Bu or Cy). (i) Mo(CO)₃(NCMe)(t-Bu-DAB). A quantity of Mo(CO)₃(NCMe)₃ was generated in situ by heating $Mo(CO)_6$ (5.0 g, 18.94 mmol) in 50 cm³ of freshly distilled acetonitrile for 36 h. Without isolating the tris(acetonitrile) product, solid t-Bu-DAB (3.20 g, 18.94 mmol) was added to the pale yellow solution. The reaction mixture was stirred at room temperature for 30 min, whereupon the solution turned dark purple and a dark blue-purple microcrystalline material separated. The solid was collected by filtration and washed with diethyl ether and hexane and dried in vacuo. A further quantity of the product was obtained by evaporating the filtrate to dryness. Recrystallization was effected from an acetonitrile-petroleum ether mixture to give dark purple crystals having a metallic luster; yield 7.07 g (96%). Found: C, 46.5; H, 6.0. Calc. for C₁₅H₂₃MoN₃O₃: C, 46.3; H, 5.9%.

(ii) $Mo(CO)_3(NCMe)(Cy-DAB)$. This product was prepared by a procedure analogous to that described in Section A(i): yield 92%.

B. Preparation of W(CO)₃(NCEt)(R'-DAB) $(\mathbf{R}' = i - \mathbf{Pr}, t - \mathbf{Bu} \text{ or } \mathbf{Cy}).$ (i) $W(\mathbf{CO})_3(\mathbf{NCEt})(i - \mathbf{Pr} - \mathbf{V})$ DAB). A 100-cm three-necked flask was charged with W(CO)₃(NCEt)₃ (2.0 g, 4.62 mmol) and *i*-Pr-DAB (0.711 g, 5.08 mmol). Addition of 25 cm³ of dichloromethane by syringe and stirring the mixture under a nitrogen atmosphere resulted in the formation of a royal blue solution. The mixture was then stirred vigorously for 2 h at ambient temperature. After this period, the reaction solution was filtered to remove a small amount of a beige insoluble material, which was subsequently discarded, and the dark blue filtrate was taken to dryness under a stream of nitrogen. The purple-blue product was recrystallized from propionitrile-petroleum ether mixtures to give shiny dark purple platelets: yield 1.77 g (83%). Found: C, 36.6; H, 4.7. Calc. for C₁₄H₂₁N₃O₃W: C, 36.3; H, 4.5%.

(ii) $W(CO)_3(NCEt)(t-Bu-DAB)$. Yield 74%. Found : C, 39.6; H, 5.7%. Calc. for $C_{16}H_{26}N_3O_3W$: C, 39.1; H, 5.1%.

(iii) W(CO)₃(NCEt)(Cy-DAB). Yield 86%. Found: C, 43.1; H, 5.3. Calc. for $C_{20}H_{29}N_3O_3W$: C, 44.2; H, 5.3%.

C. Reactions of $M(CO)_4(R'-DAB)$ (M = Mo or W) with isocyanides. (i) $Mo(CO)_3(CNCMe_3)(t-Bu-DAB)$. A mixture of $Mo(CO)_4(t-Bu-DAB)$ (1.00 g, 2.66 mmol) and 1.2 equivalents of tert-butyl isocyanide (0.34 cm³, 3.20 mmol) in 30 cm³ of toluene was stirred for 1 h at reflux. During the reaction period, the solution turned from a dark red to a royal blue. Upon cooling the reaction solution to 0°C, dark purple-blue crystals precipitated. The product was collected by filtration and washed with copious amounts of diethyl ether and petroleum ether prior to being dried *in vacuo*. An additional quantity of the product was obtained by taking the blue toluene filtrate to dryness and recrystallizing the product from acetone-diethyl ether: yield 0.92 g (80%). Found: C, 50.5; H, 7.1; N, 9.7. Calc. for $C_{18}H_{29}MON_3O_3$: C, 50.1; H, 6.8; N, 9.7%.

(ii) $Mo(CO)_3(CNMe)(t-Bu-DAB)$. Yield 54%. Found : C, 47.1 ; H, 6.0. Calc. for $C_{15}H_{23}MoN_3O_3$: C, 46.3 ; H, 5.9%.

(iii) Mo(CO)₃(CNCHMe₂)(*t*-Bu-DAB). Yield 63%. Found: C, 49.0; H, 7.3. Calc. for $C_{17}H_{27}MoN_3O_3$: C, 48.9; H, 6.5%.

(iv) $Mo(CO)_3(CNC_6H_{11})(t-Bu-DAB)$. Yield 67%. Found : C, 52.5; H, 7.2. Calc. for $C_{20}H_{31}MoN_3O_3$: C, 52.5; H, 6.8%.

(v) $Mo(CO)_3(CNxylyl)(t-Bu-DAB)$. Yield 74%. Found : C, 54.9 ; H, 5.7. Calc. for $C_{22}H_{29}MoN_3O_3$: C, 55.1 ; H, 6.1%.

(vi) $Mo(CO)_3(CNCMe_3)(i$ -Pr-DAB). Yield 58%. Found : C, 47.5; H, 6.1. Calc. for $C_{16}H_{25}MoN_3O_3$: C, 47.6; H, 6.2%.

(vii) W(CO)₃(CNMe)(*t*-Bu-DAB). Yield 73%. Found : C, 45.9; H, 5.6. Calc. for $C_{15}H_{23}MoN_3O_3$: C, 46.3; H, 5.9%.

(viii) W(CO)₃(CNCMe₃)(*t*-Bu-DAB). Yield 68%. Found: C, 41.4; H, 5.8. Calc. for $C_{18}H_{29}N_3O_3W$: C, 41.6; H, 5.6%.

(ix) $W(CO)_3(CNxylyl)(t-Bu-DAB)$. Yield 75%. Found: C, 46.9; H, 5.3. Calc. for $C_{22}H_{29}N_3O_3W$: C, 46.6; H, 5.2%.

Preparation of M(CO)₃(CNR)(R'-DAB) D. from $M(CO)_3(CNR)_3$ (M = M or W). (i) $Mo(CO)_3(CNCMe_3)(Cy-DAB)$. A quantity of $Mo(CO)_3(NCMe)_3$ was prepared by heating a mixture of $Mo(CO)_6$ (3.0 g, 11.4 mmol) and 50 cm³ of freshly distilled acetonitrile at reflux for 24 h. The reaction mixture was then allowed to cool to room temperature and Cy-DAB (2.53 g, 11.5 mmol) was added to the solution. The mixture was stirred for 15 min at ambient temperature by which time the solution had turned a royal blue color. Addition of tert-butyl isocyanide (1.25 cm³, 11.8 mmol) yielded a dark purple-blue solution upon further stirring of the mixture for 15 min. Filtration of the reaction mixture afforded an olive green insoluble material, and the filtrate was taken to dryness under reduced pressure. The purple-blue crystals which resulted were recrystallized from acetone-petroleum ether and dichloromethane-hexane mixtures: yield 4.29 g (78%). Found: C, 54.0; H, 6.7. Calc. for C₂₂H₃₃MoN₃O₃: C, 54.7; H, 6.8%.

(ii) $Mo(CO)_3(CNCMe_3)(t-Bu-DAB)$. Yield 96%. The identity of the product was confirmed by its

spectroscopic and electrochemical properties which were identical to those of an authentic sample as prepared in Section C(i).

(iii) Mo(CO)₃(CNCMe₃)(*i*-Pr-DAB). Yield 84%.

- (iv) Mo(CO)₃(CNMe)(t-Bu-DAB). Yield 75%.
- (v) Mo(CO)₃(CNCHMe₂)(Cy-DAB). Yield 78%.
- (vi) Mo(CO)₃(CNxylyl)(*i*-Pr-DAB). Yield 92%.
- (vii) Mo(CO)₃(CNxylyl)(Cy-DAB). Yield 94%.

(viii) Mo(CO)₃(CNCMe₃)(*p*-tol-DAB). Yield 32%. An alternative to the preceding procedure involved the reaction of the isolated mononitrile complexes $M(CO)_3(NCR)(R'-DAB)$ (see Sections A and B) with one equivalent of RNC (R = Me, CHMe₂, CMe₃, C₆H₁₁ or xylyl) at room temperature in deoxygenated dichloromethane. Representative experimental details for this synthetic method are described for the preparation of W(CO)₃(CNCMe₃)(*i*-Pr-DAB) from W(CO)₃(NCEt)(*i*-Pr-DAB).

(ix) W(CO)₃(CNCMe₃)(*i*-Pr-DAB). Typically, a quantity of W(CO)₃(NCEt)(*i*-Pr-DAB) (0.5 g, 1.08 mmol) was stirred in 15 cm³ of dry, deoxygenated dichloromethane at room temperature. The addition of *tert*-butylisocyanide(0.114cm³, 1.08 mmol) to the royal blue solution changed the reaction medium to a dark purple color. The mixture was stirred at room temperature for 6 h, and then taken to dryness under reduced pressure to yield small dark purple crystals. The product was washed with copious amounts of petroleum ether, and the solid then recrystallized from acetone–diethyl ether: yield 0.45 g (85%). Found: C, 39.5; H, 5.5. Calc. for $C_{16}H_{25}N_3O_3W: C, 39.2; H, 5.1\%$.

- (x) W(CO)₃(CNxylyl)(*i*-Pr-DAB). Yield 86%.
- (xi) W(CO)₃(CNCMe₃)(Cy-DAB). Yield 91%.
- (xii) W(CO)₃(CNxylyl)(Cy-DAB). Yield 94%.
- (xiii) W(CO)₃(CNC₆H₁₁)(t-Bu-DAB). Yield 85%.

E. Oxidation of Mo(CO)₃(NCMe)(t-Bu-DAB) to $[Mo(CO)_3(NCMe)(t-Bu-DAB)]PF_6$. A 25-cm³ three-necked flask was charged with $Mo(CO)_3(NCMe)(t-Bu-DAB)$ (0.5 g, 1.285 mmol) and $[Cp_2Fe]PF_6$ (0.425 g, 1.285 mmol). The addition of 10 cm³ of dry acetonitrile with stirring resulted in an immediate reaction to form a dark orange-red solution. The reaction mixture was then filtered under nitrogen to remove any insoluble materials, which were discarded, and 80 cm³ of anhydrous diethyl ether were added to the filtrate. The bright orange crystals that precipitated after about 10 min were collected by filtration and washed with copious amounts of diethyl ether before being dried in vacuo: yield 0.49 g (71%). Found: C, 34.0; H, 4.9. Calc. for C₁₅H₂₃F₆MoN₃O₃P: C, 33.7; H, 4.3%.

The air-sensitive orange solid could be recrystallized from acetonitrile-diethyl ether and dichloromethane-diethyl ether mixtures. Orangered colored solutions of the complex turned colorless almost immediately upon exposure to air.

F. Oxidations of $Mo(CO)_3(CNR)(R'-DAB)$. (i) [Mo(CO)₃(CNMe)(t-Bu-DAB)]PF₆. A 15-cm³ aliquot of freshly distilled dichloromethane was syringed into a flask containing Mo(CO)₃(CNMe)(t-Bu-DAB) (0.25 g, 0.643 mmol) and [Cp₂Fe]PF₆ (0.215 g, 0.650 mmol), whereupon the solution immediately changed from royal blue to dark redorange in color. The reaction mixture was filtered under nitrogen, and addition of 50 cm³ of anhydrous diethyl ether to the filtrate precipitated an orange solid. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. Recrystallization from dichloromethane-diethyl ether afforded bright orange crystals of the above formulation : yield 0.254 g (74%). Found : C, 33.7; H, 4.5. Calc. for C₁₅H₂₃F₆MoN₃O₃P:C, 33.7;H, 4.3%.

The solid is extremely air- and moisture-sensitive in the solid state, and solutions of the complex decompose very rapidly when exposed to the air.

(ii) $[Mo(CO)_3(CNCMe_3)(t-Bu-DAB)]PF_6$. Yield 82%.

Although the compounds $[Mo(CO)_3(CNR)(R'-DAB)]PF_6$ (R = Me or CMe₃, R' = t-Bu) could be isolated as solids, their use as starting complexes in this way was inconvenient because of their extreme air sensitivity. Accordingly, when solutions of the monocations were required they were normally generated *in situ* through the reaction of $Mo(CO)_3(CNR)(R'-DAB)$ with $[Cp_2Fe]PF_6$ in dichloromethane solution. These solutions were then used for reactions involving isocyanide and/or R'-DAB.

G. Preparation of cis, trans-[Mo(CO)₂(CNCMe₃)₂-(t-Bu-DAB)]PF₆. (i) From [Mo(CO)₃(CNCMe₃)(t-Bu-DAB)]PF₆. A dark orange-red solution of the cation $[Mo(CO)_3(CNCMe_3)(t-Bu-DAB)]PF_6$ prepared by stirring a mixture of was $Mo(CO)_3(CNCMe_3)(t-Bu-DAB)(0.60 g, 1.39 mmol)$ and [Cp₂Fe]PF₆ (0.465 g, 1.41 mmol) in 15 cm³ of freshly distilled dichloromethane at room temperature for 15 min. A mixture of tert-butyl isocyanide (0.15 cm³, 1.42 mmol) and t-Bu-DAB (0.234 g, 1.39 mmol) dissolved in 15 cm³ of dry dichloromethane was then added dropwise to the resulting solution. The orange-red solution changed to a dark red color during the addition of the reagents and CO gas evolution occurred. The reaction mixture was stirred at room temperature for 30 min, filtered, and the filtrate taken to dryness under reduced pressure. The bright red solid so obtained was washed with copious amounts of diethyl ether until the washes were colorless in order to ensure that all traces of ferrocene and unreacted Mo(CO)₃(CNCMe₃)(t-Bu-DAB) had been removed. The product was then recrystallized from dichloromethane-diethyl ether and acetone-diethyl ether mixtures: yield 0.77 g (88%). Found: C, 41.6; H, 6.6. Calc. for $C_{22}H_{38}F_6MoN_4O_2P$: C, 41.8; H, 6.1%.

(ii) From [Mo(CO)₃(NCMe)(t-Bu-DAB)]PF₆. A sample of the complex [Mo(CO)₃(NCMe)(t-Bu-DAB)]PF₆ (0.305 g, 0.571 mmol) was dissolved in 15 cm³ of freshly distilled dichloromethane, and a mixture of *tert*-butyl isocyanide (0.121 cm³, 1.15 mmol) and t-Bu-DAB (0.1 g, 0.595 mmol) dissolved in 15 cm³ of dichloromethane was then added dropwise with rapid stirring. Reaction for 30 min and a work-up and purification procedure as described in Section G(i) gave crystals of *cis*, *trans*-[Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB)]PF₆; yield 0.31 g (85%).

H. Reduction of cis, trans- $[Mo(CO)_2(CNCMe_3)_2]$ (t-Bu-DAB)]PF₆ to form cis, trans-Mo(CO)₂ (CNCMe₃)₂(t-Bu-DAB). Dry deoxygenated acetone (15 cm³) was syringed into a flask containing cis, trans-[Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB)]PF₆ (0.418 g, 0.662 mmol) and Cp₂Co (0.125 g, 0.662 mmol). The mixture was stirred at room temperature for 30 min during which time the color of the solution became turquoise blue. The solution was filtered under nitrogen to remove an olive green solid $([Cp_2Co]PF_6)$ and the clear, blue filtrate was evaporated to dryness under reduced pressure. The blue solid was recrystallized from diethyl etherpetroleum ether and dichloromethane-petroleum ether mixtures : yield 0.21 g(65%). Found : C, 53.8; H, 8.6. Calc. for C₂₂H₃₈MoN₄O₂: C, 54.3; H, 7.8%.

I. Reactions of [Mo(CO)₃(CNR)(R'-DAB)]PF₆ with isocyanides. (i) $[Mo(CO)(CNCMe_3)_4(t-Bu-$ DAB](PF₆)₂. A solution of [Mo(CO)₃(CNCMe₃)(t-Bu-DAB)]PF₆ was generated by stirring a mixture of Mo(CO)₃(CNCMe₃)(t-Bu-DAB) (0.40 g, 0.928 mmol) and [Cp₂Fe]PF₆ (0.31 g, 0.937 mmol) in 25 cm³ of dichloromethane at room temperature for 15 min. The dark red-orange solution was filtered under nitrogen, and three equivalents of tert-butyl isocyanide (0.295 cm³, 2.784 mmol) were added dropwise to the filtrate. The reaction mixture immediately turned a dark red-purple color and CO gas was evolved. It was stirred for 1 h and then taken to dryness under reduced pressure. The purple residue was extracted with diethyl ether to yield a red solid and a royal blue ethereal solution. The red solid was collected by filtration and recrystallized from dichloromethane-diethyl ether, and finally from methanol-diethyl ether to give red-orange crystals of $[Mo(CO)(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$: yield 0.38 g (45%). Found: C, 40.4; H, 6.3; N, 9.1. Calc. for $C_{31}H_{56}F_{12}MoN_6OP_2$: C, 40.7; H, 6.1; N, 9.2%.

The blue diethyl ether filtrate was evaporated to dryness under a stream of nitrogen gas and the solid recrystallized from dichloromethane-petroleum ether to give purple-blue microcrystals: yield 0.16 g (40%). This solid was identified as $Mo(CO)_3(CNCMe_3)(t$ -Bu-DAB) on the basis of its spectroscopic and electrochemical properties which were identical to those of an authentic sample [see Section C(i)].

(ii) $[Mo(CNCMe_3)_7](PF_6)_2$. The dropwise addition of four equivalents of tert-butyl isocyanide $(0.98 \text{ cm}^3, 9.285 \text{ mmol})$ to a mixture of $[Mo(CO)_3(CNCMe_3)(t-Bu-DAB)]PF_6$ (1.336) g, 2.320 mmol) {formed from Mo(CO)₃(CNCMe₃)(t-Bu-DAB) (1.0 g, 2.320 mmol) and $[Cp_2Fe]PF_6$ (0.768 g, 2.320 mmol) in 25 cm³ of dichloromethane caused the red-orange solution to change color immediately to a dark purple-blue and evolution of CO to occur. The reaction mixture was stirred at room temperature for 6 h, and the solution then taken to dryness under reduced pressure. The residue was washed with copious amounts of diethyl ether to give a yellow powder and a royal blue ether solution. The yellow product was recrystallized from dichloromethane-diethyl ether and methanoldiethyl ether before drying it in vacuo: yield 1.0 g (45%). The identity of this yellow complex as $[Mo(CNCMe_3)_7](PF_6)_2$ was confirmed by comparison of its spectroscopic and electrochemical properties with those exhibited by an authentic sample.10,11

The ether extract was evaporated to dryness to yield a quantity of $Mo(CO)_3(CNCMe_3)(t-Bu-DAB)$ (0.40 g), whose identity was confirmed by its spectroscopic and electrochemical properties.

(iii) $[Mo(CNCMe_3)_5(i-Pr-DAB)](PF_6)_2$. Dark red-purple crystals of this complex were obtained by a procedure analogous to that described in Section I(i) through the reaction between $Mo(CO)_3(CNCMe_3)(i-Pr-DAB)(0.5 \text{ g}, 1.266 \text{ mmol}),$ $[Cp_2Fe]PF_6$ (0.42 g, 1.269 mmol), and three equivalents of *tert*-butyl isocyanide (0.40 cm³, 3.79 mmol) in 15 cm³ of freshly distilled dichloromethane: yield 0.65 g (50%). Found: C, 41.9; H, 6.8. Calc. for $C_{33}H_{61}F_{12}MoN_7P_2$: C, 42.1; H, 6.5%.

The work up of the blue filtrate followed by recrystallization of the product from dichloromethane-petroleum ether gave a small quantity of $Mo(CO)_3(CNCMe_3)(i-Pr-DAB)$: yield 0.08 g (16%).

(iv) $[Mo(CO)(CNMe)_4(t-Bu-DAB)](PF_6)_2$. A brick red powder with this stoichiometry was obtained by the use of a procedure similar to that described in Section I(i) with $Mo(CO)_3(CNMe)(t-Bu-DAB)$ (0.109 g, 0.281 mmol), $[Cp_2Fe]PF_6$ (0.093 g, 0.281 mmol) and three equivalents of methyl

isocyanide $(0.50 \text{ cm}^3, 0.625 \text{ mmol})$ in 20 cm³ of dichloromethane: yield 0.10 g (48%). Characterization was based on its IR spectral and cyclic voltammetric properties which were very similar to those of its *tert*-butyl isocyanide analogue.

J. Reaction of [Mo(CO)₃(NCMe)(t-Bu-DAB)]PF₆ with tert-butyl isocyanide. $[Mo(CO)(CNCMe_3)_4]$ $(t-Bu-DAB)](PF_6)_2$. A quantity of $[Mo(CO)_3]$ $(NCMe)(t-Bu-DAB)]PF_6$ (0.823 g, 1.542 mmol) was prepared from Mo(CO)₃(NCMe)(t-Bu-DAB) (0.6 g, 1.542 mmol) and [Cp₂Fe]PF₆ (0.51 g, 1.542 mmol) in 35 cm³ of dichloromethane. Dropwise addition of five equivalents of tert-butyl isocyanide $(0.81 \text{ cm}^3, 7.710 \text{ mmol})$ to the resulting solution resulted in an immediate color change from dark red-orange to a dark purple-blue and the evolution of CO. A work up procedure identical to the one described in Section I(i) gave $[Mo(CO)(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$ (0.54 g, 38%) and Mo(CO)₃(CNCMe₃)(t-Bu-DAB) (0.37 g, 56%). These two products were identified on the basis of their spectroscopic and electrochemical properties which were identical to those exhibited by authentic samples of the compounds [see Sections C(i) and I(i)].

K. Attempted preparation of $[Mo(CNCMe_3)_5(t-Bu-DAB)](PF_6)_2$ from $[Mo(CO)(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$. A quantity of tert-butyl isocyanide (0.029 cm³, 0.274 mmol) was syringed into a stirred red-orange solution of $[Mo(CO)(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$ (0.20 g, 0.219 mmol) in 25 cm³ of dichloromethane. The reaction mixture was heated at reflux for 12 h, cooled to 0°C, and then taken to dryness under a stream of nitrogen. The yellow solid was collected, washed with water, diethyl ether and hexane, and recrystallized from acetone–diethyl ether : yield 0.13 g (61%). This product was deduced, on the basis of IR spectral and cyclic voltammetric data, to be $[Mo(CNCMe_3)_7](PF_6)_2$.^{10,11}

L. Preparation of Li[Mo(CO)₃(CNMe)(t-Bu-DAB)]. Solutions that contained the molybdenum and tungsten radical anions $[M(CO)_3(CNR)(R' DAB)]^{-}$ were prepared by the following general procedure. The tetrahydrofuran-soluble reducing agent LiEt₃BH (1.0 M in THF; 0.15 cm³, 0.150 mmol) was added dropwise to a solution of $Mo(CO)_3(CNMe)(t-Bu-DAB)$ (0.060 g, 0.154 mmol) in 5 cm³ of freshly distilled THF. The color of the solution changed almost immediately to a pale orange-yellow and gas evolution (BEt₃ and H₂) occurred as the monoanion was formed. Solutions containing the resulting molybdenum (and tungsten) radicals could be handled quite easily using conventional techniques.

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. ¹H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 spectrometer. The residual protons of acetone- d_6 $(\delta = 2.05 \text{ ppm vs TMS})$ 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. X-band ESR spectra were recorded using a Varian E-109 spectrometer.

Analytical procedures

Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

RESULTS AND DISCUSSION

Synthetic procedures and spectroscopic characterization of M(CO)₃(CNR)(R'-DAB)

Two, high-yield, synthetic methods have been devised for the synthesis of the complexes $M(CO)_3(CNR)(R'-DAB)$ (M = Mo or W; R = Me, CHMe₂, CMe₃, C₆H₁₁ or xylyl; R' = *i*-Pr, *t*-Bu, Cy or *p*-tol) as outlined by the sequence of reactions shown in eqns (1) and (2):

$$M(CO)_{6} \rightarrow M(CO)_{4}(R'-DAB)$$

$$\rightarrow M(CO)_{3}(CNR)(R'-DAB), \qquad (1)$$

$$M(CO)_{6} \rightarrow M(CO)_{3}(NCR)_{3}$$

$$\rightarrow M(CO)_{3}(NCR)(R'-DAB)$$

$$\rightarrow M(CO)_{3}(CNR)(R'-DAB). \qquad (2)$$

Representative examples, which are given in Experimental, show the generality of both procedures. Both methods are superior to that involving the reaction of $M(CO)_3(R'-DAB)(SnCl_3)Cl (M = Mo or W)$ with RNC,¹ since these latter reactions proceed (via the reductive elimination of SnCl₄) only in the cases where R' = t-Bu. As indicated in eqn (2), it is possible to isolate the blue-purple nitrile precursors $M(CO)_3(NCR)(R'-DAB)$, and this has been done for a few such derivatives (M = Mo, R = Me, R' = t-Bu or Cy; M = W, R = Et, R' = i-Pr, t-Bu or Cy).

The new complexes prepared are dark blue or purple solids. They are generally stable to atmospheric oxygen in the solid state, and dissolve in organic solvents, especially the more polar ones, imparting an intense blue to purple coloration to the solution. It should be noted that the isocyanide complexes are very stable in solution, while solutions of the nitrile complexes decompose quite rapidly (even in deoxygenated solvents), thereby complicating the measurement of their solution spectral properties.

Microanalytical data, together with ¹H NMR spectral data (recorded in acetone- d_6),* confirmed the stoichiometries of these complexes. The chemical shifts of the azomethine protons indicate that the R'-DAB ligands are in the σ , σ -bidentate coordination mode.^{12,13} Their IR spectra $\int v(CN)$ and v(CO)modes] are presented in Table 1, together with representative electronic absorption spectral data. As is often the case, the v(CN) modes for the coordinated nitrile ligand are extremely weak in some instances not seen.¹⁴ The IR spectra octahedral. diamagnetic complexes of the $M(CO)_3(CNR)(R'-DAB)$, show a single isocyanide stretching mode at $\sim 2100 \text{ cm}^{-1}$ and three intense carbonyl stretching absorptions, both in the solid state and in solution, in the region $1940-1780 \text{ cm}^{-1}$. This implies that in the isocyanide complexes the three carbonyl ligands are in a facial arrangement and that the solid-state structure of the complexes persists in solution. Likewise, the nitrile complexes exhibit similar spectral properties and hence, most likely, possess the same rigid stereochemistry. This is also the structure of the 2,2'-bipyridine complex Mo(CO)₃(NCEt)(bpy).¹⁵

The most noteworthy feature in the electronic absorption spectra of $M(CO)_3(CNR)(R'-DAB)$ (M = Mo or W) is the intense absorption in the visible region ($\lambda_{max} \sim 580$ nm) assignable to a metalto-ligand (R'-DAB) charge transfer. We find that the location and ε_{max} value of this band depends on the polarity of the solvent (solvatochromism) and the solvent shifts are comparable to those observed for the parent species $M(CO)_4(R'-DAB)$.^{16,17} An analogous metal-to-ligand charge-transfer band is found at 529 nm in the electronic absorption spectrum of $Mo(CO)_3(NCEt)(bipy)$.¹⁵

^{*} Resonances due to the isocyanide and R'-DAB ligands had the correct integrated intensities [see A. Bell, Ph.D. Thesis, Purdue University (1985)].

Table 1. Spectroscopic data for mixed isocyanide-1,4-diaza-1,3-butadiene complexes of molybdenum and tungsten

IR absorption (cm⁻¹)

	M(C	(0)	2	(CN)	Ulantennin akonntina suanten®
Complex	Nujol mull	Dichloromethane	Nujol mull	Dichloromethane	Electronic absorption spectra
Mo(CO) ₃ (NCMe)(t-Bu-DAB)	1896s, 1790s, 1771s	1914s, 1802s, 1793s	9	4	ų
Mo(CO) ₃ (NCMe)(Cy-DAB)	1891s, 1792s, 1770s	1912s, 1801s, 1790s	Ą	Ą	ų
Mo(CO) ₃ (CNMe)(t-Bu-DAB)	1910s, 1819s, 1790s	1923s, 1827s, 1798s	2168s	2159m	575 (7000), 354 (2700), 305 (sh)
Mo(CO) ₃ (CNCHMe ₂)(Cy-DAB)	1900s, 1819s, 1794s	1921s, 1846s, 1808s	2143s	2139m	574 (3800), 393 (2600), 319 (7100)
Mo(CO) ₃ (CNCHMe ₂)(t-Bu-DAB)	1902s, 1827s, 1792s	1921s, 1835s, 1798s	2141s	2139m	578 (7200), 350 (1400), 316 (sh)
Mo(CO) ₃ (CNCMe ₃)(i-Pr-DAB)	1904s, 1810sh, 1802s	1925s, 1844s, 1810s	2151s	2130m	
Mo(CO) ₃ (CNCMe ₃)(t-Bu-DAB)	1900s, 1813s, 1798s	1921s, 1835s, 1798s	2141s	2132m	579 (6900), 351 (2600), 305 (sh)
Mo(CO) ₃ (CNCMe ₃)(Cy-DAB)	1900s, 1815sh, 1806s	1923s, 1840s, 1806s	2147s	2132m	581 (7100), 355 (2100), 312 (sh)
Mo(CO) ₃ (CNCMe ₃)(p-tol-DAB)	1927s, 1858s, 1806s	1941s, 1864s, 1838s	2134s	2134m	580 (8300), 351 (2800), 305 (sh)
Mo(CO) ₃ (CNC ₆ H ₁₁)(t-Bu-DAB)	1900s, 1817s, 1794s	1921s, 1824s, 1798s	2137s	2134m	578 (3500), 392 (2400), 319 (6800)
Mo(CO) ₃ (CNxylyl)(<i>i</i> -Pr-DAB)	1906s, 1842s, 1806s	1927s, 1856s, 1817s	2087s	2089m	574 (2800), 393 (2600), 319 (7100)
Mo(CO) ₃ (CNxylyl)(t-Bu-DAB)	1900s, 1819s, 1794s	1921s, 1846s, 1808s	2097s	2087m	576 (2600), 392 (2200), 320 (6700)
Mo(CO) ₃ (CNxylyl)(Cy-DAB)	1908s, 1842s, 1810s	1925s, 1854s, 1815s	2091s	2089m	
W(CO) ₃ (NCEt)(t-Pr-DAB)	1894s, 1798s	tu	2276vw	U	u ,
W(CO) ₃ (NCEt)(t-Bu-DAB)	1887s, 1785s, 1763s	J	2270vw	5	υ
W(CO) ₃ (NCEt)(Cy-DAB)	1898s, 1798s, 1784s	υ	q	c	U
$W(CO)_3(CNMe)(t-Bu-DAB)$	1902s, 1817s, 1788s	1919s, 1837s, 1800s	2163s	2153m	582 (11,200), 350 (2400), 300 (sh)
W(CO) ₃ (CNCMe ₃)(<i>i</i> -Pr-DAB)	1900s, 1815s, 1801s	1925s, 1844s, 1813s	2149s	2128m	570 (12,800), 354 (2400)
W(CO) ₃ (CNCMe ₃)(t-Bu-DAB)	1892s, 1810s, 1792s	1918s, 1835s, 1800s	2137s	2126m	585 (10,800), 350 (2500), 310 (sh)
W(CO) ₃ (CNCMe ₃)(Cy-DAB)	1896s, 1813s, 1796s	1923s, 1842s, 1806s	2140s	2127m	
W(CO) ₃ (CNC ₆ H ₁₁)(<i>t</i> -Bu-DAB)	1894s, 1815s, 1796s	1918s, 1825s, 1800s	2134s	2130m	u
W(CO) ₃ (CNxylyl)(<i>i</i> -Pr-DAB)	1902s, 1844s, 1806s	1927s, 1858s, 1821s	2095s	2085m	570 (10,400), 389 (4700), 335 (sh)
W(CO) ₃ (CNxylyl)(t-Bu-DAB)	1892s, 1817s, 1792s	1918s, 1846s, 1810s	2091s	2085m	581 (11,100), 443 (sh), 386 (4500), 313 (sh)
W(CO) ₃ (CNxylyl)(Cy-DAB)	1904s, 1844s, 1810s	1925s, 1856s, 1819s	2085s	2084m	570 (11,500), 389 (4900), 322 (sh)
^a Data recorded from 800 to 300 nm in ^b Not observed. ^c Not measured	n dichloromethane; ε_{\max} values	$(\times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1})$ are given that the matrix of the m	ven in parenthes	ŝ	

Mixed isocyanide-1,4-diaza-1,3-butadiene complexes of molybdenum and tungsten---II

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Complex	$E_{p,a}$	$E_{1/2}(ox)$	$E_{p,c}(1)$	$E_{p,c}(2)$
Mo(CO) ₄ (<i>i</i> -Pr-DAB)	+ 1.69	+ 0.69	-1.50	window
$Mo(CO)_4(t-Bu-DAB)$	+1.76	+ 0.70	-1.47	
Mo(CO) ₄ (Cy-DAB)	+1.72	+0.67	-1.51	
$Mo(CO)_3(NCMe)(t-Bu-DAB)$	+1.33	+0.21	-1.43	1.81
Mo(CO) ₃ (NCMe)(Cy-DAB)	+1.43	+0.21	-1.55	-1.92
Mo(CO) ₃ (CNMe)(t-Bu-DAB)	+1.34	+0.31	-1.60	
Mo(CO) ₃ (CNCHMe ₂)(t-Bu-DAB)	+1.37	+0.29	-1.64	
Mo(CO) ₃ (CNCHMe ₂)(Cy-DAB)	+1.34	+0.31	1.61	-
Mo(CO) ₃ (CNCMe ₃)(<i>i</i> -Pr-DAB)	+1.25	+0.28	- 1.66	
Mo(CO) ₃ (CNCMe ₃)(t-Bu-DAB)	+1.37	+0.30	- 1.63	
Mo(CO) ₃ (CNCMe ₃)(Cy-DAB)	+ 1.38	+0.30	-1.65	
$Mo(CO)_3(CNC_6H_{11})(t-Bu-DAB)$	+1.60	+0.34	-1.59	
Mo(CO) ₃ (CNxylyl)(<i>i</i> -Pr-DAB)	+1.29	+0.35	-1.61	
Mo(CO) ₃ (CNxylyl)(t-Bu-DAB)	+1.44	+0.38	-1.61	
Mo(CO) ₃ (CNxylyl)(Cy-DAB)	+1.33	+0.35	-1.51	
$W(CO)_4(t-Bu-DAB)$	+1.82	+0.70	-1.38	
W(CO) ₃ (NCEt)(<i>i</i> -Pr-DAB)	+1.19	+0.18	-1.39	-1. 79
W(CO) ₃ (NCEt)(t-Bu-DAB)	+1.22	+0.15	-1.39	-1.84
W(CO) ₃ (NCEt)(Cy-DAB)	+1.36	+0.18	-1.37	-1.79
W(CO) ₃ (CNMe)(t-Bu-DAB)	+1.37	+0.32	-1.29	
W(CO) ₃ (CNCMe ₃)(<i>i</i> -Pr-DAB)	+1.46	+0.37	-1.62	
$W(CO)_3(CNCMe_3)(t-Bu-DAB)$	+1.37	+0.28	-1.57	
$W(CO)_3(CNC_6H_{11})(t-Bu-DAB)$	+1.45	+0.26	-1.61	
W(CO) ₃ (CNxylyl)(<i>i</i> -Pr-DAB)	+1.42	+0.42	-1.49	
W(CO) ₃ (CNxylyl)(t-Bu-DAB)	+1.35	+0.36	-1.52	
W(CO) ₃ (CNxylyl)(Cy-DAB)	+ 1.47	+0.35	-1.57	

Table 2. Cyclic voltammetric data for mixed isocyanide-1,4-diaza-1,3-butadiene complexes of molybdenum and tungsten^a

^a In V 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⁻¹.

Redox properties of $M(CO)_3(L)(R'-DAB)$ (M = Mo or W; L = RCN or RNC)

The electrochemical properties of these nitrile and isocyanide complexes are given in Table 2 along with some related data for the $M(CO)_4(R'-DAB)$ complexes taken from Ref. 1. These results are in good agreement with those expected on the basis of existing data for $M(CO)_4(R'-DAB)$ and $M(CO_3(L)(R'-DAB)$ (L = PR₃, MeCN or THF).* 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 voltammograms of $Mo(CO)_3(NCMe)(t-$ Bu-DAB) and $Mo(CO)_3(CNCMe_3)(t-$ Bu-DAB) are shown in Fig. 1. In all instances the octahedral complexes exhibit a couple $[E_{1/2}(\text{ox})]$ corresponding to a one-electron oxidation (as determined by coulometry). For sweep rates 50 to 400 mV s⁻¹, these couples are characterized by $i_{p,a}/i_{p,c} \simeq 1$ and the ratio $i_p/v^{1/2}$ was constant, in accordance with diffusion control. The potential separation between the coupled anodic and cathodic peaks, ΔE_p , is close to 75 mV for a sweep rate of 200 mV s⁻¹ and increases slightly with increase in scan rate. These properties are (with our cell configuration¹⁹) consistent with electron-transfer processes which are reversible or approach reversibility.

The tricarbonyl complexes $M(CO)_3(NCR)(R'-DAB)(M = Mo, R = Me, R' = t-Bu \text{ or } Cy; M = W, R = Et, R' = i-Pr, t-Bu \text{ or } Cy) possess a reversible oxidation at <math>ca + 0.20$ V (M = Mo or W) vs Ag-AgCl, and a second (irreversible) oxidation between +1.1 and +1.5 V. Two irreversible reductions at $E_{p,c} \sim -1.5$ and -1.9 V for M = Mo, and $E_{p,c} \sim -1.4$ and -1.8 V for M = W, are also found (Fig. 1). Similarly, the monoisocyanide complexes $M(CO)_3(CNR)(R'-DAB)$ (M = Mo or W; R = Me,

^{*} These electrochemical measurements¹⁸ were made at a platinum bead electrode in 0.1 M tetraethylammonium perchlorate-acetonitrile solutions at ambient temperatures and a scan rate of 100 mV s⁻¹. Potentials were referenced to an Ag-AgCl electrode.



Volts vs. Ag/AgCi

Fig. 1. Cyclic voltammograms (recorded at v = 200 mVs⁻¹ using a Pt-bead electrode) for 0.2 M TBAHdichloromethane solutions of :(a) Mo(CO)₃(NCMe)(*t*-Bu-DAB), (b) M(CO)₃(CNCMe₃)(*t*-Bu-DAB), and (c) [Mo(CO)(CNCMe₃)₄(*t*-Bu-DAB)](PF₆)₂.

CHMe₂, CMe₃, C₆H₁₁ or xylyl; R' = *i*-Pr, *t*-Bu or Cy) exhibit a reversible couple at ca + 0.30 V vs Ag-AgCl, and a second (irreversible) oxidation between +1.2 and +1.6 V is further observed. The existence of only one irreversible reduction process in the cyclic voltammogram of these complexes (at $E_{p,c} \sim$ -1.4 to -1.6 V) distinguishes them from the analogous nitrile species.

In comparing the $E_{1/2}$ values of the tetracarbonyl complexes $M(CO)_{4}(R'-DAB)$ with those of their nitrile or isocyanide derivatives (Table 2), we see that the $E_{1/2}$ values for the latter species are shifted to more negative potentials. This reflects the superior σ donor ability of nitriles or isocyanides and/or their poorer π -accepting ability compared to CO when bound to the group 6 metals. Thus, the nitriles and isocyanides are better able to stabilize the metal(I) oxidation state relative to the CO ligand. Indeed, the bulk electrolyses of dichloromethane solutions of several $Mo(CO)_3(L)(R'-DAB)$ complexes (L = MeCN or RNC) afforded solutions that contain 17-electron oxidized species. Furthermore, oxidation of the complexes Mo(CO)₃(NCMe)(t-Bu-DAB) and $Mo(CO)_3(CNR)(R'-DAB)$ to the corresponding monocations has been achieved

chemically by use of the rather mild oxidizing agent ferricinium hexafluorophosphate ($[Cp_2Fe]PF_6$). This procedure produced samples of the orange-red, crystalline, 17-electron compounds [Mo(CO)₃ $(NCMe)(t-Bu-DAB)]PF_6$ and $[Mo(CO)_3(CNR)]$ (t-Bu-DAB)]PF₆ (R = Me or CMe₃) with the accompanying formation of ferrocene. The generation of the analogous tungsten monocations was not possible either by use of controlled potential electrolysis or by chemical means under the conditions we employed. This presumably attests to their reactivity and/or instability in comparison to their molybdenum congeners. While the molybdenum monocations decompose very rapidly upon exposure to oxygen, their solutions can be manipulated quite easily under nitrogen.

Relative to their neutral precursors, the monocations have IR spectra in which the v(CO) modes shift to higher energy by 100–140 cm⁻¹ (Table 3). This shift, and a similar one in the case of the v(CN)modes of the RNC ligands, is expected because of the decrease in backbonding to the π^* -levels of the CO and RNC ligands.

The X-band ESR spectra of the paramagnetic 17electron species were recorded at -160° C on frozen dichloromethane solutions; the measured g values are presented in Table 3, and a spectral trace of [Mo(CO)₃(CNMe)(t-Bu-DAB)]PF₆ is shown in Fig. 2. Although some structure is apparent in the very broad signals, no semblance of hyperfine structure attributable to interaction with the coordinated nitrogens of the R'-DAB molecules is discernible.

Although the reduction processes $[E_{p,c}(1)]$ and $E_{n,c}(2)$ in Table 2] which are seen in the cyclic voltammograms of 0.2 M TBAH-dichloromethane solutions of the $M(CO)_3(L)(R'-DAB)$ complexes are irreversible electrochemically (Table 2 and Fig. 1), the 19-electron radical complexes $Li[M(CO)_3(CNR)(R'-DAB)]$ (M = Mo or W; R = Me, CMe₃ or xylyl; R' = i-Pr, t-Bu or Cy) have been generated chemically by utilizing the commercially available triethylborohydride reagent, viz. LiEt₃BH.²⁰ The attractiveness of this procedure is that only volatile by-products (H_2 and BEt_3) are formed, and the reducing agent is THF-soluble.

The resulting paramagnetic complexes have been characterized by X-band ESR spectroscopy (Fig. 2), and Table 4 summarizes the pertinent ESR data for the complexes. The ESR parameters indicate that the unpaired electron is centered mainly in the ligand π -system for all the radical anion complexes investigated; the coordination of the M(CO)₃(CNR) moiety to the radical ligand is, however, evident from the metal isotope splittings in the ESR spectra (Fig. 2 and Table 4). Further, the ESR spectral data for

	IR absorptio	on $(\mathrm{cm}^{-1})^a$	X-band ESR ^b
Complex	ν(CO)	v(CN)	gav
[Mo(CO) ₃ (NCMe)(t-Bu-DAB)]PF ₆	2024s, 1929s, 1880s	2323w, 2290w	2.207
	2027s, 1927s, 1894s ^c	$2284w^{c}$	
$[Mo(CO)_3(CNMe)(t-Bu-DAB)]PF_6$	2029s, 1936s, 1896s	2230s	2.152
	2033s, 1948s, 1911s ^c	2222m ^c	
[Mo(CO) ₃ (CNCMe ₃)(t-Bu-DAB)]PF ₆	đ	đ	2.209

Table 3. Spectroscopic properties of some [Mo(CO)₃(L)(t-Bu-DAB)]PF₆ complexes

"IR spectra recorded as Nujol mulls.

^b Recorded at -160° C in dichloromethane.

^c IR spectra recorded in dichloromethane solutions.

^d Not measured.



Fig. 2. X-band ESR spectra of :(a) $[Mo(CO)_3(CNMe)(t-Bu-DAB)]PF_6$, (b) $[Mo(CO)_2(CNCMe_3)_2(t-Bu-DAB)]PF_6$, (c) $Li[Mo(CO)_3(CNCMe_3)(Cy-DAB)]$, and (d) $Li[W(CO)_3(CNMe)(t-Bu-DAB)]$. Spectra a and b were recorded as frozen dichloromethane solutions ($-160^{\circ}C$), while spectra c and d were recorded as THF solutions at room temperature.

the complexes clearly distinguishes them from the previously characterized ligand radicals, and the radical anionic complxes K[M(CO)₄(R'-DAB)] (M = Mo or W).^{18,21,22} The most prominent features of the ESR spectra can be interpreted in terms of coupling to the diazabutadiene nitrogens, azomethine protons, and protons on the alkyl substituents (i.e. R' = *i*-Pr or Cy).

Reactivity studies

While the 18-electron neutral complexes $Mo(CO)_3(CNR)(R'-DAB)$ are unreactive toward an excess of RNC or R'-DAB, activation of these complexes by a one-electron oxidation to the monocationic 17-electron species enables further substitution chemistry to be developed. Thus, the addition of dichloromethane solutions containing one equivalent and two equivalents of *tert*-butyl isocyanide, respectively, to solutions of the redcomplexes $[Mo(CO)_3(CNCMe_3)(t-Bu$ orange DAB]PF₆ (prepared in situ) and [Mo(CO)₃ (NCMe)(t-Bu-DAB)]PF₆, gave cis, trans-[Mo(CO)₂ (CNCMe₃)₂(t-Bu-DAB)]⁺ with concomitant CO evolution. The dark blue neutral dicarbonyl cis, trans-Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB) is easily prepared by the chemical reduction of the cation using cobaltocene in acetone solution. The related

† For an acetone- d_6 solution, δ + 1.39 (s, CMe₃), + 1.62 (s, *t*-Bu) and + 8.46 (s, C—H).

2,2'-bipyridyl complex $Mo(CO)_2(CNEt)_2(bpy)$ has been assigned a *cis*, *cis*-structure on the basis of its IR spectral properties.¹⁵

The v(CO) and v(CN) modes in the IR spectra of $[Mo(CO)_2(CNCMe_3)_2(t-Bu-DAB)]^{1+,0}$ complexes again proved to be useful as a means of distinguishing between the 17- and 18-electron congeners (see Table 5). The v(CO) bands shift by between +100and $+120 \,\mathrm{cm}^{-1}$ upon changing from the zerovalent complex to the monocation and, in addition, the v(CN) absorption increases by ca 110 cm⁻¹ as the formal charge on the metal complex increases; both of these shifts reflect a decrease in the π -back donation to the CO and RNC π^* molecular orbitals. The same IR spectral pattern exists for the 18electron complex, cis, trans-Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB) and for the oxidized species, thereby indicating that no major geometrical change is associated with the redox process (Table 5). The 1 H NMR spectral properties of the neutral complex support the proposed geometry and integration of 1,4-diaza-1,3-butadiene and isocyanide resonances,[†] together with the elemental microanalyses, showed excellent agreement with the proposed stoichiometry.

The above chemical and spectral observations are in agreement with the results of electrochemical studies which were carried out on *cis*, *trans*- $[Mo(CO)_2$ (CNCMe₃)₂(*t*-Bu-DAB)]^{1+,0} in 0.2 M TBAH– dichloromethane solution (Table 5). The substitution of one carbonyl ligand by an iso-

	<u></u>	R'-DAB	(H,H) ^b					
М	CNR	R'	R ″	- A _N	A _{H(R'')}	A _{H(R')}	A _M ^c	g
Мо	CNMe	t-Bu	н	6.10	4.7	đ	2.6	1.9991
Мо	CNCMe ₃	i-Pr	Н	7.05	4.25	1.50	3.1	1.9967
Мо	CNCMe ₃	Су	н	6.70	е	e	е	1.9967
Мо	CNxylyl	i-Pr	Н٠	7.05	4.25	1.50	3.0	1.9999
Мо	CNxylyl	t-Bu	Н	7.00	4.20	đ	3.7	1.9986
Мо	CNxylyl	Cv	Н	6.80	е	е	е	1.9980
W	CNMe	t-Bu	н	6.90	4.30	đ	6.2	1.9998
W	CNCMe ₃	i-Pr	н	6.90	4.10	1.40	6.5	2.0036
W	CNxylyl	t-Bu	Н	7.00	4.20	đ	6.1	2.0014
W	CNxylyl	Су	Н	6.80	e	e	e	2.0037

Table 4. Coupling constants (A_x) (G) and g values of the radical anions Li[M (CO)₃(CNR)(R'-DAB)]^a

" Measured in THF solutions at ambient temperatures.

^bThe 1,4-diaza-1,3-butadienes, R'-N=CR''=CR''=N-R', have the general formula R'-DAB(H,H), where R'' = H.

 $^{\circ 95,97}$ Mo, 25.4% natural abundance, $I = \frac{5}{2}$; 183 W = 14.2%; $I = \frac{1}{2}$.

^d Not observed.

^e Spectra were not analyzed in detail.

							I.
	IR absorp	tions $(\text{cm}^{-1})^a$					
Complex	v(CN)	v(CO)	$E_{p,a}(\mathrm{ox})^b$	$E_{1/2}(\mathrm{ox})^b$	$E_{p,c}(\mathrm{red})^{b}$	Λ_m^c	
Mo(CO) ₂ (CNCMe ₃) ₂ (<i>t</i> -Bu-DAB)	2026s ⁴	1838s, 1773s	+1.06	-0.26	-1.83	I	I I
[Mo(CO)2(CNCMe3)2(t-Bu-DAB)]PF6	2141s ^d 2141m ^{dJ}	1939s, 1850s 1948s, 1842s ⁵	+1.06	-0.26	-1.83	137	
[Mo(CO)(CNMe)₄(t-Bu-DAB)](PF ₆) ₂	2211s, 2179sh	1905s	1	+1.39	-0.71	Ι	
[Mo(CO)(CNCMe ₃)4(t-Bu-DAB)](PF ₆)2	2186s, 2168s 2176s, 2157s ⁷	1927sh, 1896s 1919s⁄	l	+ 1.40	-0.67	230	
^{<i>a</i>} IR spectra recorded as Nujol mulls unless otherwise stab. Cyclic voltammetric data recorded in 0.2 M TBAH-dit ^{<i>b</i>} Cyclic voltammetric data recorded in 0.2 M BAH-dit ^{<i>c</i>} Values in Ω^{-1} cm ² mol ⁻¹ ; measured on 10 ⁻³ M soluti ^{<i>d</i>} This v(CN) mode has a shoulder at ~40 cm ⁻¹ to high ^{<i>e</i>} Value for $E_{1/2}$ (red) reported. ^{<i>f</i>} IR spectra recorded in dichloromethane solutions.	ated. chloromethane: values in V ions in acetonitrile at room er energy that reflects some	vs Ag-AgCl, with a Pt-b temperature. departure from non-line:	ead electrode an urity of the <i>trans</i> .	id a sweep rate Mo(C≡N—C	of 200 mV s ⁻¹ .) ₂ unit.		

Table 5. IR spectra, and cyclic voltammetric and conductivity data for isocyanide complexes derived from reactions of the monocations [Mo(CO)₃(CNR)(t-Bu-DAB)]⁺

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cyanide in Mo(CO)₃(CNR)(R'-DAB) to produce $Mo(CO)_2(CNR)_2(R'-DAB)$ causes a change in the electrochemistry. The oxidation of $Mo(CO)_2(CNR)_2(R'-DAB)$ to its monocation occurs at a lower potential [compared to that of Mo(CO)₃(CNR)(R'-DAB)], as is expected when a carbonyl ligand is replaced by a less effective π acceptor RNC ligand. Several electrochemical investigations have examined the $cis \rightleftharpoons trans$ isomerizations that occur in carbonyl derivatives of the types $Mo(CO)_4(PR_3)_2$,²³ $Mo(CO)_2(P-P)_2$ [where $\mathbf{P}-\mathbf{P} = \mathbf{P}\mathbf{h}_{2}\mathbf{P}(\mathbf{C}\mathbf{H}_{2})_{n}\mathbf{P}\mathbf{P}\mathbf{h}_{2};$ $n = 1 - 3^{24 - 26}$ and $Mo(CO)_4(carbene)_2^{27}$ following their oxidation. Particularly relevant to the present case is the conversion of cis, cis-Mo(CO)₂(CNR)₂(PR₃)₂ to the all trans-isomer upon oxidation.²⁸ We find that no such isomerization occurs when the 18-electron complex cis, trans-Mo(CO)₂(CNCMe₃)₂(t-Bu-DAB) is oxidized. The bonding constraints and electronic properties imposed by the chelating R'-DAB ligand do not favor such a stereochemical change.

The X-band ESR spectrum of the paramagnetic species, *cis*, *trans*-[Mo(CO)₂(CNCMe₃)₂(*t*-Bu-DAB)]⁺, was recorded at -160° C on a frozen dichloromethane solution (Fig. 2) and the measured g values found to be as follows: $g_1 = 2.199$, $g_2 = 2.166$, and $g_3 = 1.981$.

Three equivalents of alkyl isocyanide RNC (R = Me or CMe₃) react very rapidly with the activated complexes [Mo(CO)₃(CNR)(t-Bu-DAB)]+ at room temperature to give the seven-coordinate molybdenum(II) complex [Mo(CO)(CNR)₄(t-Bu-DAB)](PF₆)₂ (Fig. 1 and Table 5),* as well as the reduced starting complex Mo(CO)₃(CNR)(t-Bu-DAB). Disproportionation of the molybdenum(I) complex, in the presence of RNC, apparently occurs to give an intermediate, reactive, dicationic molybdenum(II) complex and the reduced product $Mo(CO)_3(CNR)(t-Bu-DAB)$: the dicationic species then reacts further with RNC to yield the final product, $[Mo(CO)(CNR)_4(t-Bu-DAB)]^{2+}$. The same products, $Mo(CO)_3(CNR)(t-Bu-DAB)$ and $[Mo(CO)(CNR)_4(t-Bu-DAB)]^{2+}$, are isolated if four equivalents of isocyanide are added to [Mo(CO)₃(NCMe)(t-Bu-DAB)]PF₆. Upon addition of four equivalents of isocyanide to the $[Mo(CO)_3(CNCMe_3)(t-Bu-DAB)]^+$ complex, the reaction proceeds to the homoleptic sevencoordinate isocyanide complex $[Mo(CNCMe_3)_7]^{2+}$ rather than to [Mo(CNCMe₃)₅(t-Bu-DAB)](PF₆)₂. In accord with this result, when [Mo(CO)

 $(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$ is reacted with *tert*butyl isocyanide (one equivalent) loss of CO and *t*-Bu-DAB occurred to give the homoleptic isocyanide complex $[Mo(CNCMe_3)_7](PF_6)_2$ as a major product.

If a different 1,4-diaza-1,3-butadiene ligand is employed, namely *i*-Pr-DAB, a similar disproportionation reaction takes place, but the final molybdenum(II) product is the dication $[Mo(CNCMe_3)_5(i-Pr-DAB)]^{2+}$, a species we have isolated previously¹ in a different study. Accordingly, the exact course of these reactions is dependent on the R'-DAB ligand used and this is supported by other work. Specifically, we have shown that complexes of the type $[Mo(CNR)_5(R' [DAB]^{2+}$ (R' = *i*-Pr or Cy) can be prepared by the action of RNC $(R = CHMe_2 \text{ or } CMe_3)$ on the seven-coordinate molybdenum(II) complexes $Mo(CO)_3(R'-DAB)(SnCl_3)Cl^1$ However, under similar conditions, the t-Bu-DAB derivative Mo(CO)₃(t-Bu-DAB)(SnCl₃)Cl undergoes reductive elimination to form the octahedral complexes $Mo(CO)_3(CNR)(t-Bu-DAB).$

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REFERENCES

- 1. A. Bell and R. A. Walton, J. Organomet. Chem. 1985, 290, 341.
- J. Casanova, Jr, R. E. Schuster and N. D. Werner, J. Chem. Soc. 1963, 4280.
- (a) W. D. Weber, G. W. Gokel and I. K. Ugi, Angew. Chem., Int. Ed. Engl. 1972, 11, 530; (b) R. E. Schuster, J. E. Scott and J. C. Casanova, Jr, Organic Synthesis. Collect. Vol. 3, p. 772. Wiley, New York (1973).
- 4. J. M. Kliegman and R. K. Barnes, *Tetrahedron* 1970, 26, 2555.
- 5. A. T. T. Hsieh and B. O. West, J. Organomet. Chem. 1976, 112, 285.
- (a) H. tom Dieck and I. W. Renk, Chem. Ber. 1971, 104, 92; (b) H. Bock and H. tom Dieck, Angew. Chem., Int. Ed. Engl. 1966, 5, 520.
- D. P. Tate, J. M. Augl and W. R. Knipple, *Inorg. Chem.* 1961, 1, 433.
- 8. G. J. Kubas, Inorg. Chem. 1983, 22, 692.
- D. N. Hendrickson, Y. S. Sohn and H. B. Gray, *Inorg. Chem.* 1971, 10, 1559.
- C. M. Giandomenico, L. H. Hanau and S. J. Lippard, Organometallics 1982, 1, 142.
- W. S. Mialki, R. E. Wild and R. A. Walton, *Inorg. Chem.* 1981, 20, 1380.
- 12. L. H. Staal, D. J. Stufkens and A. Oskam, *Inorg. Chim.* Acta 1978, **26**, 255.
- 13. H. tom Dieck, I. W. Renk and K. D. Franz, J. Organomet. Chem. 1975, 94, 417.

^{*} The ¹H NMR spectrum of $[Mo(CO)(CNCMe_3)_4(t-Bu-DAB)](PF_6)_2$ in acetone- d_6 is as follows : $\delta + 1.60$ (s, t-Bu), + 1.70 (s, CMe₃) and + 8.71 (s, C—H).

- See, for example, M. G. B. Drew, D. G. Tisley and R. A. Walton, J. Chem. Soc., Chem. Commun. 1970, 600.
- 15. J. A. Connor and C. Overton, J. Chem. Soc., Dalton Trans. 1982, 2397.
- H. tom Dieck and I. W. Renk, Angew. Chem., Int. Ed. Engl. 1970, 9, 793.
- 17. H. Bock and H. tom Dieck, Chem. Ber. 1967, 100, 228.
- H. tom Dieck and E. Kühl, Z. Naturforsch. 1982, 37B, 324.
- T. C. Zietlow, D. D. Klendworth, T. Nimry, D. J. Salmon and R. A. Walton, *Inorg. Chem.* 1981, 20, 947.
- See, for example, J. A. Gladysz, G. M. Williams, W. Tam and D. L. Johnson, J. Organomet. Chem. 1977, 140, Cl; D. Seyferth, R. S. Henderson and L.-C. Song, Organometallics 1982, 1, 125.

- K. D. Franz, H. tom Dieck, U. Krynitz and I. W. Renk, J. Organomet. Chem. 1974, 60, 361.
- 22. K. D. Franz, H. tom Dieck, K. A. Ostoja Starzewski and F. Hohmann, *Tetrahedron* 1975, **31**, 1465.
- 23. A. M. Bond, D. J. Darensbourg, E. Mocellin and B. J. Stewart, J. Am. Chem. Soc. 1981, 103, 6827.
- 24. F. L. Wimmer, M. R. Snow and A. M. Bond, *Inorg. Chem.* 1974, 13, 1617.
- 25. A. M. Bond, R. Colton and J. J. Jackowski, Inorg. Chem. 1975, 14, 2526.
- A. M. Bond, B. S. Grabaric and J. J. Jackowski, *Inorg. Chem.* 1978, 17, 2153.
- R. D. Riecke, H. Kojima and K. Öfele, J. Am. Chem. Soc. 1976, 98, 6735.
- K. A. Conner and R. A. Walton, Organometallics 1984, 2, 169.