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MIXED CARBONYL-ALKYL ISOCYANIDE COMPLEXES OF MOLYBDENUM

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Summary

The synthesis of complexes of the type $Mo(CO)_2(CNR)_2(PR_3)_2$ (R = CH_3, CMe_3 or C_6H_{11} and PR_3 = PEt_3, PPr^n_3, $PMePh_2$ or $PEtPh_2$) has been accomplished by the reaction of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ with slightly more than two equivalents of PR_3. The stereochemistry of these complexes has been deduced from IR and ^{1}H, ^{13}C and ^{31}P NMR measurements. When RNC is reacted with $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ in the presence of a small amount of $PMePh_2$, the complexes *cis*-$Mo(CO)_2(CNR)_4$ are formed in 20—25% yield together with $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_4]^+$ (R = CMe_3 or C_6H_{11}). The latter cations have been isolated as their $B(C_6H_5)_4^-$ salts. The formation of *cis*-$Mo(CO)_2(CNR)_4$ under these conditions supports the proposal that the phosphine-assisted allyl chloride elimination is an important mechanism in the reactions of phosphines with derivatives of the type $(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Cl$. The X-ray photoelectron spectra of certain complexes of the types $Mo(CO)_2(CNR)_2(PR_3)_2$ and *cis*-$Mo(CO)_2(CNR)_4$ have been recorded and the results are discussed briefly.

Introduction

As a consequence of our studies on the "shake-up" satellite phenomena associated with the X-ray photoelectron spectra (XPS) of alkyl and aryl isocyanide complexes of chromium, molybdenum and tungsten [1,2] we became interested in both homoleptic isocyanide complexes (e.g. $[Mo(CNCH_3)_7]^{2+}$) [3,4] as well as mixed carbonyl-isocyanides (e.g. *cis*-$Mo(CO)_2(CNBu^t)_4$) [5]. In the course of this work [2] we had cause to synthesize molybdenum complexes of the type $Mo(CO)_2(CNR)_2(PR_3)_2$. In the present report we describe the synthesis and

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spectroscopic characterizations of several such derivatives. We have also investigated the preparation of several complexes of the type *cis*-$Mo(CO)_2(CNR)_4$ by the reductive elimination of allyl chloride from $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$, a procedure previously studied by King and Saran [5]. During this particular aspect of our work we discovered that the compound $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4]BPh_4$ could be isolated as a major product in the reaction which leads to the formation of *cis*-$Mo(CO)_2(CNBu^t)_4$.

Experimental

Starting materials

$Mo(CO)_6$ was a gift of the Climax Molybdenum Company. tert-Butyl isocyanide, cyclohexyl isocyanide, tertiary phosphines, and solvents were used as received from commercial sources. Methyl isocyanide, and sometimes tert-butyl and cyclohexyl isocyanide, were made by literature procedures [6,7]. $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ was prepared by tom Dieck's method [8], in which a mixture of $Mo(CO)_6$ and allyl chloride is refluxed in acetonitrile. Complexes of the type $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ were obtained using King's method [9] as recounted below. ^{13}C-enriched $Mo(CO)_6$ was made by photolytically generating $Mo(CO)_5(THF)$ and transferring this solution to an evacuated flask to which ^{13}CO gas was then admitted at 1 atm pressure. After stirring this mixture for about an hour until the yellow color due to the THF complex was greatly diminished, the solvent was stripped off and the product purified by sublimation. This procedure was repeated to bring the enrichment up to 10—20%, a level which was estimated from the infrared spectrum of the enriched $Mo(CO)_6$.

Reaction procedures

All solvents were deoxygenated by purging with N_2 and reactions were carried out under a nitrogen atmosphere. Liquid chromatography columns were also deoxygenated. Solid products could be filtered, washed, and weighed in air but should be stored under N_2 and kept shielded from unnecessary exposure to light in order to prolong their lifetime.

A) $Mo(CO)_2(CNR)_2(PR_3)_2$ compounds. The general procedure for these reactions is as follows. Approximately 0.5 g of the acetonitrile complex $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ was dissolved in 20 ml of CH_2Cl_2 at room temperature. An amount of RNC in slight excess of two equivalents was added causing the orange solution to turn deep red immediately as the labile acetonitrile ligands were displaced by isocyanide [5]. The resulting isocyanide complex $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ was precipitated by reducing the volume of the solution and adding hexane, filtered off, washed with hexane, and then was redissolved in about 20 ml of CH_2Cl_2. A two-fold excess of the appropriate phosphine was added and the solution stirred all day or overnight at room temperature. At the end of this period the CH_2Cl_2 solution was reduced in volume to 5—10 ml, and then placed on a 15 × 2 cm florisil column. The column was then eluted with dichloromethane/hexane (8/1). The yellow band was collected and the solvent stripped off. The resulting yellow oil was purified by precipitation from methanol or methanol/dichloromethane solutions through the addition of water. Yields of these products were 40—70%. Microanalytical data for an assortment of complexes of this type are given in Table 1. In addition to the compounds listed in Table 1, $Mo(CO)_2(CNC_6H_{11})_2(PEt_3)_2$ was obtained as a yellow oil by this procedure but could not be crystallized. It was identified by its IR and NMR spectral properties. Samples of $Mo(CO)_2(CNCH_3)_2(PMePh_2)_2$ were also prepared but were found by IR spectroscopy to be contaminated with small amounts of $Mo(CO)_2(CNCH_3)_4$. It was found later that such $Mo(CO)_2(CNR)_4$ impurities arise only when the $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ compounds are not isolated from their reaction solution prior to reaction with phosphine, i.e., when there is excess of isocyanide present during the reductive elimination.

B) $Mo(CO)_2(CNR)_4$ compounds and $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4]BPh_4$. A small quantity of methyldiphenylphosphine (0.1—0.2 ml) was added to a CH_2Cl_2 solution containing 0.5 g $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ and a two-fold excess of CNR. After stirring this mixture for 18 h at room temperature it was chromatographed and the yellow band collected as described in A. The products $Mo(CO)_2(CNR)_4$, where R = CH_3, Bu^t, and C_6H_{11}, were obtained in 20—25% yield (Table 1). Analytically pure $Mo(CO)_2(CNCH_3)_4$ was obtained by evaporating the solvent after elution from the chromatography column, while $Mo(CO)_2(CNBu^t)_4$ was obtained by crystallization upon the addition of water to a methanol/dichloromethane solution. However, when the cyclohexyl isocyanide derivative was recrystallized using the same solvent system, it was found by NMR to be contaminated with a small amount of a phosphine-containing species, probably $Mo(CO)_2$-

TABLE 1

MICROANALYTICAL DATA FOR ISOCYANIDE COMPLEXES OF MOLYBDENUM

Compound	Yield (%)	Analysis. Found (calcd.) (%)		
		C	H	N
$Mo(CO)_2(CNCH_3)_2(PEt_3)_2$	59	45.95 (45.97)	7.58 (7.71)	6.02 (5.96)
$Mo(CO)_2(CNBu^t)_2(PEt_3)_2$	40	52.10 (51.98)	8.72 (8.72)	4.97 (5.05)
$Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$	69	56.37 (56.42)	9.68 (9.47)	4.55 (4.39)
$Mo(CO)_2(CNBu^t)_2(PMePh_2)_2$	68	63.73 (63.51)	5.99 (6.17)	3.67 (3.90)
$Mo(CO)_2(CNC_6H_{11})_2(PPr^n_3)_2$	48	58.95 (59.12)	9.37 (9.34)	3.93 (4.06)
$Mo(CO)_2(CNC_6H_{11})_2(PEtPh_2)_2$	57	66.09 (66.16)	6.83 (6.56)	3.29 (3.51)
$Mo(CO)_2(CNCH_3)_4$	22	38.27 (37.99)	4.07 (3.83)	17.72 (17.72)
$Mo(CO)_2(CNBu^t)_4$	24	54.74 (54.54)	7.42 (7.49)	11.50 (11.56)
$Mo(CO)_2(CNC_6H_{11})_4$	20	61.17 (61.21)	7.53 (7.53)	9.21 (9.52)
$[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4][B(C_6H_5)_4]$	45	70.77 (70.58)	7.63 (7.53)	7.00 (6.86)

$(CNC_6H_{11})_2(PMePh_2)_2$ or $Mo(CO)_2(CNC_6H_{11})_3(PMePh_2)$. Upon triturating the bright yellow precipitate with a small amount of methanol the intensely yellow-colored contaminant dissolved, leaving behind the pale yellow solid $Mo(CO)_2(CNC_6H_{11})_4$. This was recrystallized from dichloromethane/methanol.

Following the elution of the yellow $Mo(CO)_2(CNR)_4$ band, the column was next eluted with MeOH in an attempt to isolate other products of the reaction. In the case of $R = Bu^t$, an orange band was collected. Excess $NaBPh_4$ dissolved in MeOH was added and large orange crystals separated upon the addition of water and cooling. NMR and IR spectra and microanalytical data (Table 1) support the formulation $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4]BPh_4$. The XPS spectrum of this complex showed the absence of chlorine. An orange band was also eluted from the reaction which produced $Mo(CO)_2(CNC_6H_{11})_4$ but, in this case, only an impure orange oil was obtained. Its NMR and IR spectra indicated that it was the cyclohexyl isocyanide complex $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNC_6H_{11})_4]BPh_4$. In the case of methyl isocyanide, no other products could be eluted from the column; only a black, oily material remained after eluting the $Mo(CO)_2(CNCH_3)_4$.

C) Attempted synthesis of $Mo(CO)_2(CNC_6H_{11})_2(PMe_3)_2$. When the procedure described in A for the preparation of the $Mo(CO)_2(CNR)_2(PR_3)_2$ compounds was carried out using trimethylphosphine, the expected yellow band of $Mo(CO)_2(CNR)_2(PMe_3)_2$, analogous to that of other complexes of this type as described in A, was not present on the florisil column. Methanol eluted most of the material on the column as an orange band. Upon addition of sodium tetraphenylborate to the eluate, an orange oil separated immediately. This oil did not redissolve in methanol. Attempts to solidify it by trituration with various solvents and attempts to crystallize it failed. Its IR and NMR spectra indicated that it may be $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNC_6H_{11})_2(PMe_3)_2]BPh_4$.

Physical measurements

Infrared spectra were recorded on a Beckman IR-12 instrument. A Perkin-Elmer R32 NMR spectrometer was used for the ^1H NMR spectra, while Varian CFT-20 and XL-100 spectrometers were used for ^{13}C and ^{31}P spectra, respectively. $CDCl_3$ or acetone-d_6 were used as solvents for these measurements. X-Ray photoelectron spectra (XPS) were recorded on a Hewlett-Packard 5950A ESCA spectrometer. Microanalyses were performed by Dr. C.S. Yeh, Purdue University.

Whereas a healthy ^{13}C NMR signal in the carbonyl region was obtained with a 10—20% ^{13}CO-enriched sample of $Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$ (0.1—0.3*M* solution in acetone-d_6) after one hour (using a pulse width of 3 μsec and a pulse delay of 0.5 sec), we were unable to obtain signals from unenriched samples. Use of small flip angles, long pulse delays, added $Cr(acac)_3$ to speed up relaxation times, and thousands of pulses failed to produce a signal from the unenriched samples.

Results and discussion

In the reactions between tertiary phosphines and the acetonitrile complex $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$, complexes of the types *cis*-$Mo(CO)_2(PR_3)_4$ or $Mo(CO)_2(NCCH_3)_x(PR_3)_{4-x}$ ($x = 1$ or 2) are produced following the reductive elimination of allyl chloride [8,10—12]. The stoichiometry of the final product from this reductive elimination is dependent upon the nature of the phosphine, being controlled by both the steric and electronic (basicity) properties of the phosphine [12]. In the case of the mixed acetonitrile-phosphine complexes $Mo(CO)_2(NCCH_3)_x(PR_3)_{4-x}$, other ligands (L) can be substituted for the labile acetonitrile to afford a variety of compounds of the type $Mo(CO)_2(L)_2(PR_3)_2$, where R = Bu^n or Ph [10]. We felt that it should be possible to form the isocyanide derivatives $Mo(CO)_2(CNR)_2(PR_3)_2$ without being restricted to the phosphines PBu^n_3 and PPh_3 by reversing the order of the two reactions. That is, first the acetonitriles of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ are replaced by ligands (i.e. isocyanides) which do not favor the elimination of allyl chloride, and then the resulting complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ are reacted with phosphines. At first these reactions were carried out without isolating the intermediate isocyanide complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$, i.e. the phosphine was added a few minutes after the addition of the appropriate isocyanide. Consequently, excess isocyanide was present while the reductive elimination reaction was proceeding. When $Mo(CO)_2(CNCH_3)_2(PMePh_2)_2$ was prepared in this way small amounts of $Mo(CO)_2(CNCH_3)_4$ contaminated the desired product. The identification of this minor side product led us to study the formation of the $Mo(CO)_2(CNR)_4$ compounds (vide infra). Another problem caused by the presence of excess isocyanide in the reaction mixture is that these ligands tend to polymerize and form black tars which may interfere with the chromatographic separations. Both of these problems are circumvented by isolating the appropriate $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ compound and washing away the excess isocyanide before reaction with phosphine.

While we did not attempt to prepare all possible complexes of the type $Mo(CO)_2(CNR)_2(PR_3)_2$ for the range of isocyanide and phosphine ligands which we used, there seems little doubt that most can be prepared by this method. The microanalytical data and infrared spectra of the complexes we prepared are presented in Tables 1 and 2. The ^1H NMR spectra of all the derivatives appeared to be normal and confirmed the absence of any residual allyl resonances *. Details of the ^1H NMR spectra will not be discussed further.

The infrared spectra in the ν(CO) and ν(CN) regions (Table 2) are in accord with *cis*-arrangements of CO and CN groups. ^{13}C and ^{31}P NMR spectral measurements were also employed to assist in the assignment of the stereochemistry of the $Mo(CO)_2(CNR)_2(PR_3)_2$ compounds. Singlets were observed in the ^{31}P spectra of $Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$ and $Mo(CO)_2(CNBu^t)_2(PMePh_2)_2$ at 23 and 31 ppm, respectively, downfield from 85% H_3PO_4. The proton-decoupled ^{13}C spectrum of a sample of $Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$ which had been prepared from ^{13}CO-enriched $Mo(CO)_6$, contained a 1 : 2 : 1 triplet 221.3 ppm downfield from TMS with a coupling constant of 9 Hz. The triplet indicates splitting by two equivalent phosphorus nuclei, which is consistent with the singlet obtained in the ^{31}P NMR spectra.

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* For example, an acetone-d_6 solution of $Mo(CO)_2(CNCH_3)_2(PEt_3)_2$ exhibited its $CNCH_3$ resonance at δ 3.30 ppm (singlet) while the resonances of the PEt_3 ligands were at δ 1.10 (pentet) and 1.65 ppm (multiplet). For $Mo(CO)_2(CNBu^t)_2(PEt_3)_2$, the resonances were at δ 1.43 (singlet, $CNBu^t$), 1.15 (pentet) and 1.73 ppm (multiplet).

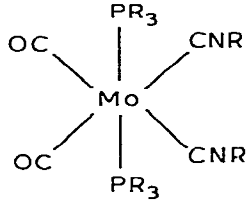
TABLE 2

INFRARED ACTIVE ν(CO) AND ν(CN) MODES

Compound	Medium [a]	ν(CO) (cm^{-1}) [b]	ν(CN) (cm^{-1}) [b]
$Mo(CO)_2(CNCH_3)_2(PEt_3)_2$	NM	1845s, 1795s	2120s, 2095s
$Mo(CO)_2(CNCH_3)_2(PMePh_2)_2$	NM	1857s, 1804s	2156m, 2126m-s
$Mo(CO)_2(CNBu^t)_2(PEt_3)_2$	NM	1874s, 1840s, ~1800m-s	2105m, 2048m-s
$Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$	NM	1854s, 1803s	2108m, 2050m
	CH_2Cl_2	1842s, 1792s	2105m, 2050m
$Mo(CO)_2(CNBu^t)_2(PMePh_2)_2$	NM	1855s, 1810s	2125m, 2100m
	CH_2Cl_2	1860s, 1808s	2118m-w, 2100m-w, 2065m-w [d]
$Mo(CO)_2(CNC_6H_{11})_2(PEt_3)_2$	NM	~1860s, ~1820s	~2100s, ~2050m
$Mo(CO)_2(CNC_6H_{11})_2(PEtPh_2)_2$	NM	1857s, 1810s	2128m-w, 2100m
	CH_2Cl_2	1868s, 1818s	2138m-w, 2102m-w
cis-$Mo(CO)_2(CNCH_3)_4$ [c]	NM	1850s, 1800s	2180m, 2142m-s, 2095s
cis-$Mo(CO)_2(CNBu^t)_4$ [c]	NM	1873s, 1830s	2145m, 2100m, 2060(sh), 2016m-s
cis-$Mo(CO)_2(CNC_6H_{11})_4$	NM	1868s, 1820s	2144m, 2100(sh), 2070m, 2036s
	CH_2Cl_2	1870s, 1823s	2152m-w, 2100(sh), 2080(sh), 2045s
$[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4]BPh_4$	NM	1895s	2195m-s, 2157s
	CH_2Cl_2	1905m	2180w, 2138m

[a] NM = Nujol mull. [b] ±5 cm^{-1}. [c] Data in good agreement with that published by King and Saran [9] for a sample of this complex obtained using a different synthetic procedure. [d] This absorption is believed to be due to an impurity.

An empirical rule for ^{13}C—^{31}P coupling constants of molybdenum(0) carbonyl-phosphine compounds is that a phosphine *trans* to a carbonyl produces a large coupling constant of about 40 Hz, while a phosphine *cis* to a carbonyl ligand produces a much smaller coupling constant (9 Hz) [13]. Since the case where all like ligands are *trans* to each other is ruled out by the infrared spectra (only one band each would then be expected for ν(CO) and ν(CN)), the NMR data favor I as being the structure of these complexes.



(I)

King and Saran [9] were the first to show that alkyl isocyanides replace the two acetonitrile ligands in $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ to form $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$. Such substitution reactions occur very rapidly at room temperature. Under more vigorous conditions (i.e. reflux and/or long reaction times) these reactions proceed further to produce an assortment of products, the specific reaction course being dependent upon the nature of the alkyl isocyanide [9]. In the case of methyl and ethyl isocyanides the complexes *cis*-$Mo(CO)_2(CNR)_4$ are produced in low yield (R = methyl, 18%; R = ethyl, 10%) but with other isocyanides (R = iso-propyl, tert-butyl, neopentyl and cyclohexyl) either decomposition occurs (R = iso-propyl and cyclohexyl) or different products are formed, namely, $(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_3Cl$ in the case of R = tert-butyl and neopentyl and $[(t\text{-}BuNC)_4MoCl]_2$ [9]. These variations are not well understood since there is no obvious explanation in terms of trends in the properties of R.

Of particular interest to us were the observations [9] concerning the conversion of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ to *cis*-$Mo(CO)_2(CNR)_4$ by an excess of alkyl isocyanide, i.e. that the reaction occurs with some isocyanides but not with others. We also tried the reactions between $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ and RNC in CH_2Cl_2 at room temperature for prolonged periods but these produced only black intractible tars. However, we have discovered this reaction can be affected with all the isocyanides (CH_3NC, Bu^tNC and $C_6H_{11}NC$) if carried out at room temperature in the presence of a small quantity of phosphine (we used $PMePh_2$ for this purpose). By this means we have produced the methyl, tert-butyl and cyclohexyl isocyanide derivatives of the type *cis*-$Mo(CO)_2(CNR)_4$. The spectral properties of these molecules (Table 2) are those which are expected [5,9] *.

We believe that our observations are in accord with the currently favored mechanism for the reductive elimination of C_3H_5Cl [10,12]. In the conversion

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* ^1H NMR spectra were routinely used to characterize these compounds. As King and Saran have noted [5], the spectrum of $Mo(CO)_2(CNBu^t)_4$ contains two closely spaced singlets at δ 1.36 and 1.39 ppm due to the two non-equivalent pairs of tert-butyl isocyanide ligands. We find no distinction between these pairs of ligands in the spectra of the methyl and cyclohexyl derivatives.

of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(PR_3)_2Cl$ to *cis*-$Mo(CO)_2(PR_3)_4$, Friedel et al. [10] have proposed that phosphine first attacks the allyl group and that this is followed by the dissociation of the allyl phosphonium ion, as opposed to a mechanism involving $\eta^3 \to \eta^1$ rearrangement of the allyl group. Clark et al. [12] have also argued for this from kinetic studies which revealed decreased rates of *cis*-$Mo(CO)_2(PR_3)_4$ formation with decreasing solvent polarity. In the reaction between $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ and mixtures of PR_3 and RNC, phosphine attack on the bound allyl group again assists in the elimination of allyl chloride. If PR_3 is in excess, then *cis*-$Mo(CO)_2(PR_3)_4$ is formed as a major product, while *cis*-$Mo(CO)_2(CNR)_4$ is favored in an excess of RNC. By carefully controlling the PR_3 and RNC stoichiometries in these reactions we can also produce $Mo(CO)_2(CNR)_2(PR_3)_2$ (vide supra). The mechanism for the formation of *cis*-$Mo(CO)_2(CNR)_4$ from $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ in the absence of phosphine [9] remains unclear at present.

Although the yields of *cis*-$Mo(CO)_2(CNR)_4$ as prepared by our procedure are only 20—25%, it is likely these can be improved considerably by carefully varying the proportions of RNC and $PMePh_2$ in the reaction mixtures. We have chosen not to carry out such a study at this time since there are other available synthetic procedures. Thus *cis*-$Mo(CO)_2(CNBu^t)_4$ has been prepared from the 1,3-cyclohexadiene complex $(C_6H_8)_2Mo(CO)_2$ in 72% yield [5] and also by the $CoCl_2 \cdot 2\,H_2O$-catalyzed reaction between *fac*-$Mo(CO)_3(CNBu^t)_3$ and Bu^tNC [14].

In the room temperature reaction between $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ and RNC in the presence of a small quantity of $PMePh_2$, the reactions involving Bu^tNC and $C_6H_{11}NC$ afforded, in addition to *cis*-$Mo(CO)_2(CNR)_4$, the cations $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_4]^+$ (isolated as their BPh_4^- salts) in moderate yield. Since these reactions were carried out with an excess of RNC over $PMePh_2$ it is perhaps not surprising that there is a competitive non-reductive elimination pathway. These cations are apparently closely related to the $(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_3Cl$ compounds which King and Saran [9] found could be formed from $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ upon their further reaction with RNC. The allyl resonances in the ^1H NMR spectrum of $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNBu^t)_4]BPh_4$ consisted of a broad singlet at $\delta \sim 5.0$ ppm, a doublet at δ 3.22 ppm with 9 Hz coupling, and a doublet at δ 2.56 ppm with 12 Hz coupling.

As mentioned in the Introduction, our interest in molecules of the types $Mo(CO)_2(CNR)_2(PR_3)_2$ and *cis*-$Mo(CO)_2(CNR)_4$ arose from our studies on the satellite structure in the XPS of isocyanide complexes of the Group VI elements [1,2]. Data for these mixed carbonyl-isocyanide complexes are reported herein, that for other isocyanides will be described elsewhere [2]. Since we discovered that these complexes suffered extensive radiation damage upon irradiation at room-temperature with an X-ray beam power of 1000 W, we recorded measurements under conditions (T = 190 K, beam power 600 W) which eliminated, as far as we could ascertain, such decomposition. Primary core electron binding energies of the three complexes which we studied in detail are presented in Table 3. The values of the Mo 3*d* binding energies are in accord with these complexes being dicarbonyl derivatives of zero-valent molybdenum [15]. The most noteworthy features in the N 1*s*, O 1*s* and C 1*s* spectra are the appearance of satellites, to the high binding energy side of the primary peaks,

TABLE 3

XPS CORE ELECTRON BINDING ENERGIES OF MIXED CARBONYL-ISOCYANIDE COMPLEXES OF MOLYBDENUM [a]

Complex	Mo $3d_{5/2}$ [b]	N 1*s*	O 1*s*	P $2p_{3/2}$
cis-$Mo(CO)_2(CNCH_3)_4$	226.7 (1.4)	399.0 (2.0)	531.7 (2.5)	—
$Mo(CO)_2(CNBu^t)_2(PPr^n_3)_2$	226.9 (1.5)	399.0 (1.7)	531.9 (1.9)	130.3
$Mo(CO)_2(CNC_6H_{11})_2(PPr^n_3)_2$	227.1 (1.3)	399.3 (1.5)	532.3 (1.8)	130.6

[a] Binding energies are referenced to a C 1*s* binding energy of 285.0 eV for carbon contaminant in *cis*-$Mo(CO)_2(CNCH_3)_4$ and for the organic substituents in $Mo(CO)_2(CNR)_2(PPr^n_3)_2$; full-width half maximum values for the Mo $3d_{5/2}$, N 1*s* and O 1*s* peaks are given in parentheses. [b] Mo $3d_{3/2}$ peak located at 3.1 eV to higher binding energy.

which are probably associated with transitions which are predominantly Mo(*d*) → CO(π^*) or CNR(π^*) in type [1,16,17]. These satellites are at ΔE = 4.1—4.4 eV for N 1*s* and 5.2—5.5 eV for O 1*s* and therefore resemble closely the positions of satellites in the XPS of homoleptic carbonyl and isocyanide complexes [1,2,16,17]. The values of the intensity ratios for the satellite and primary photolines ($I_s/I_p \sim 0.2$—0.3) are also similar to those reported for molecules such as $Mo(CO)_6$ [16] and $[Mo(CNCH_3)_7](PF_6)_2$ [1]. This argues for a similarity in bonding and in the origin of the satellite features. In the case of the C 1*s* spectra, the satellite structure (centered at $\Delta E \sim 4.5$ eV) is broader and less well defined than that associated with the N 1*s* and O 1*s* peaks. The reason for this is that C 1*s* "shake-up" satellites are associated both with the CO and CNR ligands, and accordingly this gives rise to a more complex spectrum. The C 1*s* spectra of these three complexes are also different in another way. In the case of *cis*-$Mo(CO)_2(CNCH_3)_4$ the primary C 1*s* photoline at 285.8 eV is assigned to the overlap of the C 1*s* energies of the cyano and methyl carbons of CH_3NC and the carbon of CO, while the intense band centered at 285.0 eV in the XPS of $Mo(CO)_2(CNR)_2(PR_3)_2$ contains, additionally contributions from the carbon atoms of the tert-butyl and cyclohexyl groups of the CNR ligands plus the propyl groups of the phosphines. No attempt was made to deconvolute these complex (although relatively narrow) C 1*s* band envelopes.

References

1 P. Brant, W.S. Mialki and R.A. Walton, J. Amer. Chem. Soc., 101 (1979) 5453.
2 W.S. Mialki and R.A. Walton, Manuscript in preparation.
3 C.T. Lam, M. Novotny, D.L. Lewis and S.J. Lippard, Inorg. Chem., 17 (1978) 2127.
4 P. Brant, F.A. Cotton, J.C. Sekutowski, T.E. Wood and R.A. Walton, J. Amer. Chem. Soc., 101 (1979) 6588.
5 R.B. King and M.S. Saran, Inorg. Chem., 13 (1974) 74.
6 R.E. Schuster, J.E. Scott and J. Casanova, Jr., Org. Syn., 46 (1966) 75.
7 W.P. Weber, G.W. Gokel and I.K. Ugi, Angew. Chem. Int. Ed. Engl., 11 (1972) 530.
8 H. tom Dieck and H. Friedel, J. Organometal. Chem., 14 (1968) 375.
9 R.B. King and M.S. Saran, Inorg. Chem., 13 (1974) 2453.

10 H. Friedel, I.W. Renk and H. tom Dieck, J. Organometal. Chem., 26 (1971) 247.
11 B.J. Brisdon and K.E. Paddick, J. Organometal. Chem., 149 (1978) 113.
12 D.A. Clark, D.L. Jones and R.J. Mawby, J. Chem. Soc., Dalton, (1980) 565.
13 G.M. Bodner, Inorg. Chem., 14 (1975) 2694.
14 M.O. Albers, N.J. Coville, T.V. Ashworth, E. Singleton and H.S. Swanepoel, J. Organometal. Chem., 199 (1980) 55.
15 B.J. Brisdon, W.S. Mialki and R.A. Walton, J. Organometal. Chem., 187 (1980) 341.
16 G.M. Bancroft, B.D. Boyd and D.K. Creber, Inorg. Chem., 17 (1978) 1008.
17 M.B. Hall and D.E. Sherwood, Jr., Inorg. Chem., 18 (1979) 2323.