

oration of some of the hexane and cooling led to the precipitation of purple crystals. These were filtered to yield 0.7 g (0.57 mmol, 63% yield based on Co) of $\text{Cp}_2\text{Zr}[\text{OCCo}(\text{CO})_2]_2$ identified by comparison of its NMR and IR spectra with those previously published.³

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in THF. $\text{Cp}_2\text{Ti}(\text{CO})_2$, 0.50 g (2.14 mmol), was dissolved in 50 mL of THF. $\text{Co}_2(\text{CO})_8$, 0.36 g (1.07 mmol), was added as a solid to the above solution, and gas evolution was noted by foaming of the reaction mixture. Infrared analysis of the reaction mixture indicated, in addition to bands due to $\text{Co}_2(\text{CO})_8$, a very strong absorption at 1890 cm^{-1} , indicative of the $\text{Co}(\text{CO})_4^-$ species. The solution was stirred at room temperature for 3 h. Pentane was slowly added to the reaction mixture to precipitate 0.65 g (1.32 mmol, 62% yield) of a blue-green crystalline solid identified as $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$ on the basis of the following information. IR (THF solution): 1890 cm^{-1} . IR (toluene solution): 2010, 1915, 1750 cm^{-1} . Due to the lability of the THF molecules, a satisfactory elemental analysis could not be obtained. However, the single-crystal X-ray structure did confirm the composition.⁴

Reaction between $(\text{Cp}_2\text{TiCl})_2$ and $\text{TiCo}(\text{CO})_4$. $(\text{Cp}_2\text{TiCl})_2$, 1.0 g (2.34 mmol), was dissolved in 75 mL of THF, and the $\text{TiCo}(\text{CO})_4$ (1.76 g, 4.68 mmol) was added as a solid. The reaction mixture was stirred at room temperature for 18 h, at the end of which time there was a white precipitate of TiCl . The mixture was filtered, and the blue-green filtrate was diluted with pentane to precipitate 1.5 g (3.03 mmol, 65%) of a blue-green crystalline solid identical in all respects with the material synthesized from $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ described above.

Reaction between $\text{Cp}^*\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane. $\text{Cp}^*\text{Ti}(\text{CO})_2$, 0.5 g (1.34 mmol), was dissolved in 50 mL of hexane and the solution filtered to remove any insoluble material. Likewise, $\text{Co}_2(\text{CO})_8$, 0.46 g (1.34 mmol) was dissolved in 50 mL of hexane and the solution filtered. The two solutions were combined, stirred, and then allowed to stand undisturbed. After about 1 h, crystal formation was evident. After 18 h, the mixture was filtered and 0.31 g of a green, crystalline solid was isolated. After 48 h, an additional 0.24 g of product was isolated. The total yield was 0.55 g (1.12 mmol, 83% yield) of $[\text{Cp}^*\text{TiOCCo}(\text{CO})_3]_2$, identified on the basis of the following data. Anal. Found (calcd for $\text{C}_{24}\text{H}_{30}\text{CoO}_4\text{Ti}$): C, 58.3 (58.9); H, 5.81 (6.19); Ti, 9.97 (9.79); Co, 11.87 (12.04). IR (ν_{CO} , Nujol mull): 2020 (m), 1942 (s), $1835\text{ (m cm}^{-1})$. An attempt was made to obtain the X-ray crystal structure of this complex.⁵ Due to poor crystal quality the structure was not able to be refined completely, but the dimeric nature of this complex was confirmed.

Reaction between $\text{Cp}^*\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$ and $\text{Co}_2(\text{CO})_8$ in Hexane. $\text{Cp}^*\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$, 0.20 g (0.59 mmol), was dissolved in 50 mL of

hexane. $\text{Co}_2(\text{CO})_8$, 0.20 g (0.58 mmol), was added to the solution. A green precipitate formed immediately. The precipitate was filtered out, washed with hexane, and dried to yield 0.22 g (0.45 mmol, 78% yield) of $[\text{Cp}^*\text{TiOCCo}(\text{CO})_3]_2$, identical with the material formed by using $\text{Cp}^*\text{Ti}(\text{CO})_2$ as starting material.

Reaction between $\text{Cp}^*\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Toluene. $\text{Cp}^*\text{Ti}(\text{CO})_2$, 0.5 g (1.34 mmol), was dissolved in 50 mL of toluene. To the above solution was added, 0.23 g (0.67 mmol) of $\text{Co}_2(\text{CO})_8$ as a solid. An infrared spectrum of the reaction solution at this point indicated that all of the $\text{Co}_2(\text{CO})_8$ had been consumed with a significant portion of the $\text{Cp}^*\text{Ti}(\text{CO})_2$ remaining, so an additional 0.23 g of $\text{Co}_2(\text{CO})_8$ was added. The reaction mixture was stirred for 18 h. The solvent was removed under reduced pressure, and the residue was washed with hexane, leaving 0.66 g (1.0 mmol, 75% yield) of $\text{Cp}^*\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, identified on the basis of the following information. Anal. Found (calcd for $\text{C}_{28}\text{H}_{30}\text{Co}_2\text{O}_8\text{Ti}$): C, 51.33 (50.92); H, 4.41 (4.59); Co, 17.40 (17.85); Ti, 7.71 (7.25). IR (ν_{CO} , Nujol mull): 2050 (s), $1850\text{ (m cm}^{-1})$. $^1\text{H NMR}$ (C_6D_6): δ 1.67 ppm.

Thermolysis of $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$. $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, 1.0 g (0.9 mmol), was dissolved in 50 mL of xylene, and the solution was heated to reflux for 4 h. The reaction mixture was cooled, and the xylene was removed at reduced pressure. The residue was extracted with hexane, and the hexane was removed to yield 0.21 g of a dark red oil, identified as $\text{CpCo}(\text{CO})_2$ by comparison of its IR and NMR spectra with those of an authentic sample. Based on the number of available Cp rings in the system, this represents a 64% yield of $\text{CpCo}(\text{CO})_2$. The hexane-insoluble material was not characterized.

Reaction between $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$ and PPh_3 in Toluene. $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$, 0.5 g (1.01 mmol), was dissolved in 60 mL of toluene. To this solution was added 0.34 g (1.34 mmol) of PPh_3 as a solid. The solution immediately changed from green to red-brown, and after 10 min, a red-brown precipitate had formed. The mixture was allowed to stir for 3 h, and then it was filtered to collect 0.26 g (0.32 mmol, 64% yield based on Co) of $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$, identified by comparison of its IR spectrum with that of authentic material. An infrared spectrum of the filtrate showed only absorptions due to $\text{Cp}_2\text{Ti}(\text{CO})_2$.

Reaction between $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$ and PPh_3 . $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, 0.30 g (0.33 mmol), was dissolved in 50 mL of toluene. To this solution was added, 0.5 g (1.9 mmol) of PPh_3 as a solid. After a few minutes, a red-brown solid precipitated from solution. This solid was collected, washed with hexane, and dried to yield 0.65 g (0.8 mmol, 81% yield based on Co) of $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$. Infrared analysis of the solution showed only the presence of $\text{Cp}_2\text{Ti}(\text{CO})_2$.

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Multinuclear NMR Studies of Molybdenum and Tungsten Carbonyl Isocyanide Complexes¹

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$\text{M}(\text{CO})_{6-n}(\text{CNR})_n$ ($n = 0-6$) complexes ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = 2,6$ -dimethylphenyl, *tert*-butyl, cyclohexyl, isopropyl) have been synthesized. Depending on the R group of the isocyanide ligand, four or six carbonyl groups in $\text{M}(\text{CO})_6$ can be replaced. The NMR properties of the atoms in these complexes have been studied. The metal centers, observed by ^{95}Mo or ^{183}W NMR, show increased deshielding with the substitution of carbonyl ligands by isocyanide ligands. ^{95}Mo NMR serves as an excellent tool for the identification of mixtures of these compounds and was useful to monitor the reactions. The nitrogen in the isocyanide ligand, observed by ^{14}N NMR spectroscopy, gets more deshielded when the isocyanide is coordinated to the metal center, but with further substitution, the nitrogen becomes more shielded again. The ^{14}N chemical shift of an isocyanide ligand trans to a carbonyl ligand differs slightly from the chemical shift of an isocyanide ligand trans to another isocyanide ligand in the tetrasubstituted complex. The ^{13}C NMR signal of the CNR carbon becomes more deshielded with an increasing number of isocyanides present in the complex. CNR carbons trans to carbonyl groups are more shielded than CNR carbons trans to isocyanides. With the successive substitution of carbonyl groups by isocyanides, the electronic absorption bands in the UV-vis region shift toward longer wavelengths; i.e., the color of the compounds changes from white to orange-red.

Introduction

A number of papers have been published containing ^{13}C ,^{2,3} ^{14}N ,^{4,5} or ^{17}O ⁵ NMR data on molybdenum(0) and tungsten(0)

carbonyl isocyanide complexes. The data available so far are limited to mono- to trisubstituted complexes, and no NMR data for the metal nuclei in these complexes have been published.

Albers and co-workers^{6,7} discovered a convenient route to

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Table I. Elemental Analyses

compd	calcd			found		
	% C	% H	% N	% C	% H	% N
Mo(CO) ₂ (dmpi) ₄ ^a	67.45	5.36	8.28	65.85	5.40	7.92
Mo(CO)(dmpi) ₅	70.85	5.82	8.98	70.76	5.85	8.92
Mo(dmpi) ₆	73.44	6.18	9.52	73.35	6.19	9.51
Mo(CO) ₂ (cyhi) ₄	61.22	7.54	9.56	59.49	7.43	9.02
Mo(CO) ₂ (ipi) ₄	50.46	6.60	13.08	49.62	6.46	12.70
Mo(CO) ₂ (tbui) ₄	54.53	7.50	11.56	54.41	7.56	11.52
W(CO) ₂ (dmpi) ₄	59.69	4.75	7.32	58.35	4.81	7.02
W(CO)(dmpi) ₅	63.67	5.23	8.07	63.62	5.49	8.17
W(dmpi) ₆	66.80	5.61	8.65	66.68	5.62	8.63

^aThis sample contained ~10% trisubstituted product.

synthesize M(CO)_{6-n}(CNR)_n (*n* = 0–6) complexes by using PdO as a catalyst. With this method, we were able to obtain a complete series of molybdenum and tungsten complexes for NMR studies. Within the last few years, multinuclear NMR has become a valuable tool for the characterization and identification of transition-metal compounds. Atoms in different parts of the molecule can be observed. NMR spectra of metal nuclei provide an excellent tool to study the metal centers directly. It has been shown with ⁹⁵Mo NMR, for example, that small changes in the coordination sphere cause pronounced changes in the NMR chemical shift of the metal center.⁸ The replacement of a hydroxy oxygen by a mercapto sulfur in an otherwise identical complex causes deshielding of the molybdenum nucleus by about 200 ppm.⁹ Geometric isomers and diastereomers can also be distinguished quite easily.¹⁰ Multinuclear NMR spectroscopy can replace or complement other methods to characterize compounds. NMR data that show the effect of the complete exchange of one ligand by another in two-ligand complexes are rare. In this work we used ⁹⁵Mo, ¹⁸³W, ¹⁴N, and ¹³C NMR spectroscopy to observe the chemical shift changes that occur in different parts of the molecule when the carbonyl ligands in M(CO)₆ are sequentially replaced by isocyanide ligands.

Experimental Section

All experiments were performed under argon, the solvents were dried and distilled prior to use, and the products were stored at –5 °C in a drybox. Cyclohexyl (cyhi), *tert*-butyl (tbui), and isopropyl isocyanides (ipi) were purchased from Strem Chemicals, 2,6-dimethylphenyl isocyanide (dmpi) was purchased from Fluka, palladium(II) oxide, and hexacarbonylmolybdenum(0) and hexacarbonyltungsten(0) were purchased from Aldrich. The ligands, the palladium(II) oxide, and the metal hexacarbonyls were used without further purification.

The molybdenum and tungsten complexes were synthesized according to the method of Albers et al.^{6,7} by refluxing the metal hexacarbonyl with the appropriate equivalents of ligand in toluene with PdO used as catalyst. The tetra-, penta-, and hexasubstituted complexes were also synthesized with M(CO)₆ (M = Mo, W) and the corresponding equivalents of ligand, not with M(CO)₃(CNR)₃ as described in ref 6. The crude products were recrystallized in a hexanes/dichloromethane mixture. For molybdenum, the mono- to trisubstituted complexes were refluxed for 10 minutes, the tetrasubstituted compounds were obtained after refluxing from 15 min (dmpi) to 19 h (tbui). The pentasubstituted complex (dmpi) was refluxed for 1.5 h and the hexasubstituted complex (dmpi) for 2 h. In the reactions with cyhi, tbui, and ipi, no more than four carbonyl groups could be replaced with isocyanides.

The reaction times for the tungsten complexes were significantly longer. The mono- to trisubstituted compounds were refluxed for several hours; the tetrasubstituted complex was refluxed for 1 day, the pentasubstituted complex for 2 days, and the hexasubstituted complex for 4 days.

The identities of the mono- to trisubstituted complexes were confirmed by comparing the IR and ¹³C NMR data with the literature data; the

Table II. ⁹⁵Mo NMR Chemical Shifts^a

compd	chem shift, ppm			
	R = <i>tert</i> -butyl	R = isopropyl	R = cyclohexyl	R = 2,6-dimethylphenyl
Mo(CO) ₅ CNR	–1850	–1850	–1853	–1848
<i>cis</i> -Mo(CO) ₄ (CNR) ₂	–1825	–1825	–1831	–1825
<i>fac</i> -Mo(CO) ₃ (CNR) ₃	–1783	–1784	–1793	–1786
<i>cis</i> -Mo(CO) ₂ (CNR) ₄	–1716	–1726	–1729	–1715
Mo(CO)(CNR) ₅				–1626
Mo(CNR) ₆				–1525

^aReference 2 M Na₂MoO₄ in D₂O, basic; solvent CH₂Cl₂.

Table III. ¹³C and ¹⁴N NMR Chemical Shifts for Isocyanide Ligands

ligand	chem shift, ppm		ref
	¹³ C ^a (CNR)	¹⁴ N ^b (CNR)	
methyl isocyanide		–218 (8)	4, 23
ethyl isocyanide		–203 (8)	4, 23
isopropyl isocyanide	153.5 (4.8)	–194 (10)	this work
<i>n</i> -butyl isocyanide	155.4 (5.1)	–210 (10)	this work
<i>tert</i> -butyl isocyanide	152.4 (4.5)	–186 (10)	this work
cyclohexyl isocyanide	153.8 (5.3)	–197 (10)	this work
benzyl isocyanide	157.4 (4.7)	–212 (10)	this work
2,6-dimethylphenyl isocyanide	167.7 (6.2)	–206 (10)	this work
morpholinoethyl isocyanide	156.4 (5.6)	–211 (15)	this work

^aIn CDCl₃; triplet, coupling constant in Hz in parentheses.

^bReference nitromethane, neat; line width in Hz in parentheses; solvent CH₂Cl₂.

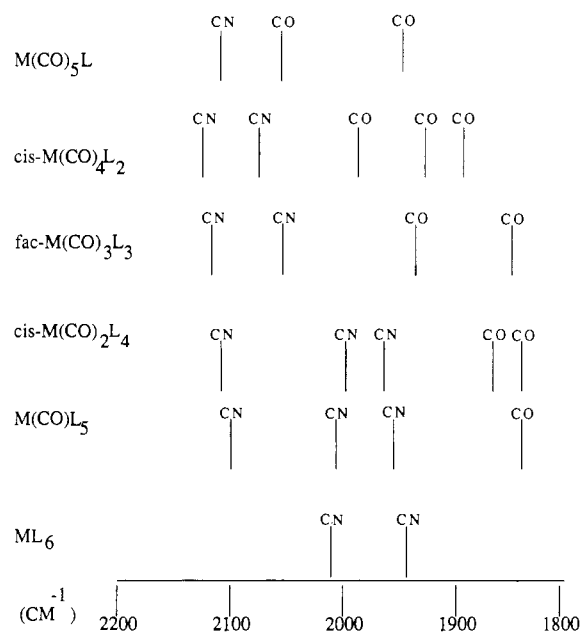


Figure 1. IR frequency diagram for M(CO)_n(CNR)_{6-n} complexes (M = Mo, W) according to ref 6.

identities of the tetra- to hexasubstituted complexes were established by elemental analysis (Table I).

IR spectra were measured on a Nicolet 5XSB FT-IR spectrometer in a NaCl IR solution cell. CH₂Cl₂ was used as solvent.

The NMR spectra were measured on an IBM NR 300-MHz NMR spectrometer. For the ¹³C NMR spectra, a 5-mm dual ¹H/¹³C probehead was used, ¹⁴N and ⁹⁵Mo NMR spectra were measured on a 10-mm broad-band probehead (¹⁰⁹Ag-³¹P) with digital tuning, and the ¹⁸³W NMR spectra were obtained with a standard selective tungsten probehead. For the ¹³C NMR spectra the solvent, CDCl₃, was used as an internal reference; for the other nuclei external standards were used as references: ¹⁴N, nitromethane, neat; ⁹⁵Mo, 2 M Na₂MoO₄ in D₂O, basic; ¹⁸³W, saturated Na₂WO₄ in D₂O, basic. The concentrations of the solutions were about 0.1 M except for ¹⁸³W NMR measurements, where generally higher concentrations or saturated solutions were used. The electronic spectra were measured on a Beckman 5260 spectrophotometer.

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Table IV. ^{14}N NMR Chemical Shifts^a

compd	chem shift, ppm				
	R = <i>tert</i> -butyl	R = isopropyl	R = cyclohexyl	R = 2,6-dimethyl-phenyl (dmp)	W complex (R = dmp)
$\text{Mo}(\text{CO})_5\text{CNR}$	-180 (10)	-188 (20)	-191 (20)	-200 (50)	-202 (30)
<i>cis</i> - $\text{Mo}(\text{CO})_4(\text{CNR})_2$	-182 (20)	-190 (20)	-193 (20)	-202 (80)	-203 (80)
<i>fac</i> - $\text{Mo}(\text{CO})_3(\text{CNR})_3$	-184 (30)	-193 (30)	-196 (40)	-202 (100)	-203 (100)
<i>cis</i> - $\text{Mo}(\text{CO})_2(\text{CNR})_4$	-183 (90)	-193 (50)	-196	-196 (200)	-206 (200)
	-187 (70)	-194 (40)	-198 ^b		
$\text{Mo}(\text{CO})(\text{CNR})_5$				-203 (330)	-197 (420)
$\text{Mo}(\text{CNR})_6$				-197 (350)	-197 (500)

^a Samples in CH_2Cl_2 ; reference nitromethane, neat; line widths in Hz in parentheses. ^b Peaks not separated well enough to determine line widths

Table V. ^{13}C NMR Data^a

compd	chem shift, ppm							
	OC-M-CO		OC-M-CNR		OC-M-CNR		RNC-M-CNR	
	Mo	W	Mo	W	Mo	W	Mo	W
$\text{M}(\text{CO})_6$	201.6	191						
$\text{M}(\text{CO})_5(\text{CNR})$	203.6	194.0	206.5	196.4	165.7	155.1		
<i>cis</i> - $\text{M}(\text{CO})_4(\text{CNR})_2$	206.0	196.7	209.5	199.8	169.8	159.5		
<i>fac</i> - $\text{M}(\text{CO})_3(\text{CNR})_3$			212.2	202.7	173.6	163.6		
<i>cis</i> - $\text{M}(\text{CO})_2(\text{CNR})_4$			215.0	205.7	177.1	167.5	181.0	170.9
$\text{M}(\text{CO})(\text{CNR})_5$			217.1	208.3	180.5	171.0	184.8	175.1
$\text{M}(\text{CNR})_6$							185.0	175.5

^a In CDCl_3 ; R = 2,6-dimethylphenyl.

Table VI. ^{13}C NMR Data^a

compd	OC-M-CO			OC-M-CNR			OC-M-CNR			RNC-M-CNR		
	R1 ^b	R2 ^b	R3 ^b	R1	R2	R3	R1	R2	R3	R1	R2	R3
$\text{Mo}(\text{CO})_6$		201.64										
$\text{Mo}(\text{CO})_5(\text{CNR})$	203.9	203.9	203.9	207.1	206.5	207.0	149.9 ^c	150.9 ^c	151.2 ^c			
<i>cis</i> - $\text{Mo}(\text{CO})_4(\text{CNR})_2$	206.6	206.5	206.6	211.0	210.8	210.7	154.4 ^c	154.7 ^c	155.9 ^c			
<i>fac</i> - $\text{Mo}(\text{CO})_3(\text{CNR})_3$				214.3	213.9	213.9	158.8	158.7	159.9			
<i>cis</i> - $\text{Mo}(\text{CO})_2(\text{CNR})_4$				217.6	217.0	217.2	163.7	163.1	164.1	173.3	170.8	171.6

^a in CDCl_3 . ^b R1 = *tert*-butyl, R2 = isopropyl, R3 = cyclohexyl. ^c Triplet.

Results

The data obtained in this work are presented in Tables I–VI, and Figure 1. Tables II–VI and Figure 1 are introduced at appropriate points in the section that follows.

Discussion

Synthesis. With the ligands used in this work, complete substitution of six carbonyl ligands in $\text{M}(\text{CO})_6$ to form $\text{M}(\text{CNR})_6$ was only possible with dmpi, a ligand with an aryl R group. The other isocyanides with aliphatic R groups (cyhi, tbui, ipi) only replaced up to four carbonyl groups. Isocyanide ligands are considered to be more basic than carbonyl ligands. They are also slightly weaker π -acceptors than carbonyl ligands² and therefore donate more electron density to the metal center. With an aromatic R group participating in the metal to ligand π -bonding, enough electron density is removed from the metal to allow complete substitution. The aliphatic R groups cannot participate in the metal to ligand π -bonding, and therefore, not enough electron density is removed to allow complete substitution. When the isocyanide ligand is introduced into the carbonyl complex, the metal–carbon bond of the carbonyl group trans to the isocyanide ligand is strengthened. As a result of this only *cis* and *fac* isomers are isolated. The CO stretching frequencies in the IR spectrum are lowered as expected (Figure 1).

Even though stoichiometric amounts of starting material were used for the syntheses of all complexes, mixtures instead of pure products were frequently obtained, especially for the higher substituted compounds. It was quite difficult to monitor the progress of the substitution by infrared spectroscopy since both the CO and the CN stretching frequencies occur in the same region and overlap. We therefore tried to use NMR spectroscopy to identify the reaction mixtures. For the molybdenum compounds ^{95}Mo NMR was a good method to monitor the reactions. The line widths of the $\text{Mo}(\text{CO})_{6-n}(\text{CNR})_n$ compounds are narrow,

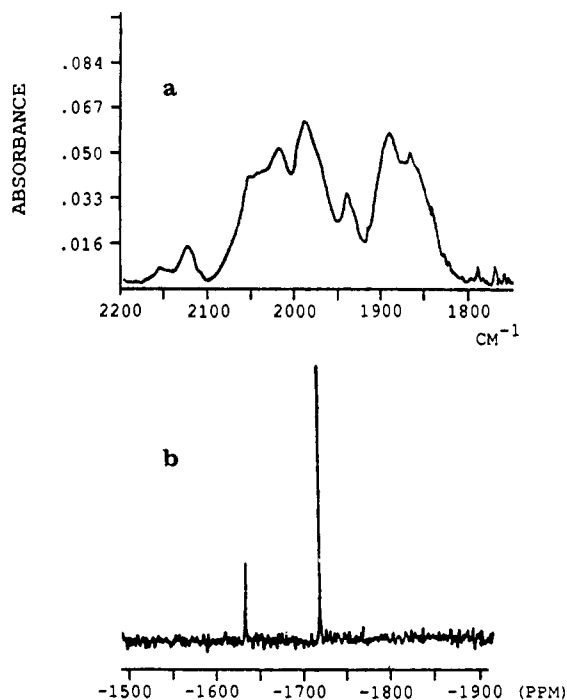


Figure 2. Mixture of $\text{Mo}(\text{CO})_2(\text{CNR})_4$ and $\text{Mo}(\text{CO})(\text{CNR})_5$ in CH_2Cl_2 : (a) IR spectrum; (b) ^{95}Mo NMR spectrum.

around 10 Hz, and spectra are obtained rapidly. Figure 2a shows the IR spectrum of a reaction mixture and Figure 2b shows the ^{95}Mo NMR spectrum of the same solution. The IR spectrum does not allow an immediate identification of the compounds in solution whereas the ^{95}Mo NMR spectrum shows the presence of two

species, Mo(CO)₂(dmpi)₄ and Mo(CO)(dmpi)₅.

Using molybdenum NMR to monitor the reactions, we were able to obtain pure products. The reaction times for the tetra- to hexasubstituted compounds were significantly shorter than indicated in the literature.⁶ Refluxing a stoichiometric mixture for the hexasubstituted dmpi complex yielded the product after 2 h compared to 24 h suggested in the literature. When the reaction mixture is refluxed longer, the product peak in the NMR spectrum decreases again. During the synthesis of the penta-substituted dmpi complex, even though stoichiometric amounts of the reactants were present, some hexasubstituted complex was formed as well.

⁹⁵Mo NMR. The ⁹⁵Mo NMR chemical shift range of the molybdenum carbonyl isocyanide compounds stretches from -1856 (Mo(CO)₆) to -1525 ppm (Mo(dmpi)₆) (Table II), a region typical for Mo(0) compounds.⁸ The molybdenum center is deshielded with each substitution. The first isocyanide causes deshielding of only 3–8 ppm. With further substitution the deshielding increases, up to 101 ppm for the last step. An almost identical deshielding pattern of the ⁹⁵Mo nucleus was found for Mo(CO)_{6-n}(P(OMe)₃)_n (*n* = 0–6) compounds,^{8,11–16} the only other complete series with two monodentate ligands studied so far. In an early ⁹⁵Mo NMR paper,¹¹ a chemical shift of -1752 ppm and a line width of 130 Hz were reported for Mo(CO)₅(CNMe₂Ph) in CDCl₃. According to our data, this value cannot be correct since all the monosubstituted complexes show deshielding of less than 10 ppm when compared to Mo(CO)₆ (CNMe₂Ph probably is dmpi).

The line widths of the ⁹⁵Mo NMR signals are about 10 Hz. For the penta- and hexasubstituted dmpi complexes, line widths of 20 and 40 Hz are observed, probably due to an increase in the correlation time, τ_c .

The R group of the isocyanide ligand does not have a large effect on the ⁹⁵Mo NMR chemical shift. The cyhi complexes with the largest aliphatic R group are slightly more shielded than the other compounds.

The deshielding of the ⁹⁵Mo nucleus by the isocyanides is small compared to that by other ligands. When two carbonyl groups in Mo(CO)₆ are replaced by other monodentate ligands to form Mo(CO)₄L₂, deshielding of 31 ppm is found for dmpi, 29 ppm for trimethyl phosphite,^{12,13} 300 ppm for triphenylphosphine,^{12,13} 549 ppm for acetonitrile,¹² and 805 ppm for pyridine.¹⁷ The largest deshielding of 826 ppm is achieved with a bidentate ligand, 2-phenylazopyridine (2-pap).¹⁸ The Mo(2-pap)₃ complex has the most positive chemical shift known to date for a Mo(0) complex, +1502 ppm.

For a theoretical understanding of the chemical shifts the Ramsey equation ($\sigma = \sigma^d + \sigma^p$), which separates the shielding, σ , into a diamagnetic (σ^d) and a paramagnetic (σ^p) term, is generally used.¹⁹ The paramagnetic term is the dominant factor in heavy nuclei such as ⁹⁵Mo²⁰

$$\sigma^p = (-\mu_0 e^2 \hbar^2 / 6\pi m^2 \Delta E) (\langle r^{-3} \rangle_{np} P_\mu + \langle r^{-3} \rangle_{nd} D_\mu)$$

where *np* and *nd* refer to the valence p and d electrons, *P_μ* and *D_μ* represent the electron imbalance about the nucleus, and ΔE is the average electronic excitation energy. With an increasing number of isocyanide ligands the color of the complexes changes from white to orange-red; i.e., ΔE becomes smaller. This causes the paramagnetic shielding term, which has a negative sign, to become larger, and the shielding decreases. The relationship between the λ_{\max} of the complexes and the ⁹⁵Mo NMR chemical shifts for this series is not linear. We have no data to estimate the values of *P_μ* or *D_μ*, and therefore, the contributions of *P_μ*, *D_μ*, and ΔE to give the observed chemical shift cannot be determined.

¹⁸³W NMR. For the tungsten compounds ¹⁸³W NMR was not a convenient method to identify reaction mixtures since the receptivity of ¹⁸³W is about 50 times lower than that of ⁹⁵Mo.²¹ Long relaxation delays between pulses are necessary for the data acquisitions from this dipolar nucleus, whereas no relaxation delays are necessary for the quadrupolar ⁹⁵Mo nucleus. ¹³C NMR was used for a first identification of the tungsten products. Without a fast method to determine the products in the reaction mixture, the reaction times could not be determined accurately. They were significantly longer than those for molybdenum (Experimental Section).

Reproducible ¹⁸³W NMR spectra were only obtained for the penta- and hexasubstituted complexes in CDCl₃ (W(CO)(dmpi)₅, -3139 ppm; W(dmpi)₆, -2918 ppm). W(CO)₆ has a chemical shift of -3486 ppm in CH₂Cl₂.²⁴ These data show that the ¹⁸³W nucleus like the ⁹⁵Mo nucleus becomes more deshielded with an increasing number of isocyanide ligands present. The chemical shift ratio of ¹⁸³W/⁹⁵Mo is 1.9. Ratios of this order are generally found when ¹⁸³W and ⁹⁵Mo NMR chemical shifts are compared.⁸ No ¹⁸³W NMR data are in the literature for higher substituted compounds except for *trans*-W(CO)₂(P(OMe)₃)₄ (-3207 ppm¹⁴).

¹⁴N NMR. The isocyanide nitrogens are easily observed by ¹⁴N NMR. They absorb around -200 ppm (Table III).^{4,22,23} There is a certain amount of confusion in the ¹⁴N literature concerning the chemical shift values. Different references with varying standard concentrations are used. Some authors give a positive chemical shift sign to compounds that absorb downfield from the reference; others assign a negative chemical shift sign in the same situation. We follow here the procedure used for most nuclei that chemical shifts upfield from the reference have a negative sign and chemical shifts downfield from the reference have a positive sign.

The isocyanide nitrogen becomes deshielded by 6 ppm when one ligand is coordinated to molybdenum (Table IV). The deshielding is only 4 ppm in the tungsten analogue. Upon further substitution, the nitrogen becomes more shielded, but the chemical shift changes are minimal compared to those of the metal centers. For the tetrasubstituted complexes, two distinct peaks are observed, 1–4 ppm apart, for the two different environments of the isocyanide ligands, *trans* to CO and *trans* to each other. No two peaks could be distinguished for the dmpi complexes because of the larger line widths. The shielding pattern can also not be seen as clearly in the dmpi complexes. This may be due to the aromatic R group, but the precision of the chemical shift values also decreases with increasing line widths (± 3 ppm for line widths from 200 to 500 Hz⁸). In [Mo(CNR)₇]²⁺ complexes the isocyanide nitrogen is considerably more deshielded (-156 ppm, R = *tert*-butyl).²⁵

Bennett and co-workers, who recently published ¹⁴N data for the mono- to trisubstituted tungsten complexes with one aliphatic ligand, *tert*-butyl isocyanide, and one aromatic ligand, *p*-tolyl isocyanide, found the same trend for their compounds.⁵ They claim that the ¹⁴N nucleus in an aryl isocyanide complex is 14–18 ppm more shielded than that in an alkyl isocyanide complex. A

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comparison of the ^{14}N chemical shifts of several isocyanide ligands (Table III) shows that ligands with aliphatic R groups such as methyl, ethyl, *n*-butyl, or morpholinoethyl isocyanide have chemical shifts equal to those with aromatic R groups. The ^{14}N chemical shifts do not change significantly after coordination, and the magnitude of the change is only slightly influenced by the nature of the R group.

The line widths of the ^{14}N NMR signals increase with an increasing number of isocyanide ligands in the complex. This increase can be correlated with the size of the R group. For a quadrupolar nucleus, the line width, $\Delta\nu_{1/2}$, can be expressed as²⁶

$$\Delta\nu_{1/2} = (\pi T_{2q})^{-1} = \frac{1}{(3\pi/10)(2I + 3/I^2(2I - 1))(e^2q_{zz}Q/h)^2(1 + \eta^2/3)\tau_c}$$

where Q is the nuclear quadrupole moment, q the local electric field gradient, and η the asymmetry parameter for q ($\eta = (q_{yy} - q_{xx})/q_{zz}$). More ligands with large R groups increase the correlation time, τ_c , which is directly proportional to the line width. The effect is smaller for the ^{95}Mo nucleus, where a significant increase in the line width is only observed for the penta- and hexasubstituted complexes.

^{13}C NMR. The ^{13}C NMR spectra show that the carbonyl carbons trans to another carbonyl group are deshielded by about 3 ppm, respectively, when the first and second isocyanide are coordinated (Tables V and VI). Carbonyl groups trans to isocyanide ligands are deshielded by about 3–4 ppm compared to the carbonyl groups trans to each other in the same complex. These carbons are also deshielded by about 3 ppm with each substitution.

The ^{13}C NMR signal of the CNR carbon is split into a triplet by nitrogen. The coupling constants range from 4.5 to 6.2 Hz (Table III). When coordinated to the metal, the CNR carbon becomes shielded by 2–3 ppm in the Mo complexes and by about 12 ppm in the W complexes (Tables V and VI). Each subsequent substitution deshields by 3–4 ppm. The C–NR coupling constants increase from 5 Hz in the free ligand to about 16 Hz in the monosubstituted complex. In the disubstituted complex, coupling constants around 14 Hz are found. These values agree with those reported for $\text{Mo}(\text{CO})_5(\text{cyhi})$ and $\text{Mo}(\text{CO})_4(\text{cyhi})_2$ earlier.² For the trisubstituted and higher substituted complexes and for all dmpi complexes, no coupling was observed.

The tetrasubstituted complexes show two CNR ^{13}C NMR signals, 4–10 ppm apart, one for isocyanide trans to isocyanide and the other for isocyanide trans to carbonyl. Comparing the peak intensities of the tetrasubstituted dmpi complex with the pentasubstituted dmpi complex allows the assignment of the more shielded peak to the isocyanide trans to the carbonyl group. The CNR carbons bound to tungsten are generally 10 ppm more shielded than those bound to molybdenum.² In the hexasubstituted complexes the CNR ^{13}C NMR signals are less deshielded and have broader line widths.

In isocyanides with aliphatic R groups, the ^{13}C NMR signal of the CNCR' carbon (R' = R group without the carbon attached

to the nitrogen) is also split into a triplet by nitrogen. The coupling constants are 5.1 Hz for tbui, 5.3 Hz for cyhi, and 5.8 Hz for ipi. These values are similar to the coupling constants found for the CNR carbons. When the first isocyanide with an aliphatic R group is bound to the metal, the CNCR' carbon becomes deshielded by about 3 ppm. As the number of isocyanide ligands increases, the CNCR' carbons become more shielded in increments smaller than 0.5 ppm. This parallels the trend found for nitrogen, and is contrary to the trend observed for the CNR carbon. While the C–NR coupling constants increase from 5 to 16 Hz, when the first isocyanide is coordinated, the CN–CR' coupling constants remain almost unchanged, 5.3 Hz for tbui, 4.7 Hz for cyhi, and 5.8 Hz for ipi. No splitting of the ^{13}C NMR CNCR' peak by nitrogen is detected in the disubstituted and higher substituted complexes.

Chemical shift changes of 1 ppm or less are observed for the other carbons in the aliphatic R groups when the number of isocyanide ligands in the complex increases. Two peaks are observed for each carbon in the tetrasubstituted complexes.

The CNCR' carbon in dmpi is deshielded by less than 0.5 ppm when the ligand is bound to Mo or W. With subsequent substitution the CNCR' carbon becomes more shielded as seen for the aliphatic carbons. No CN–CR' coupling was observed for the free or coordinated ligand. In the benzyl isocyanide ^{13}C NMR spectrum, no splitting of the CNCR' carbon was detected either. All dmpi carbons show two peaks in the tetrasubstituted compounds. Small side peaks are observed in the pentasubstituted complexes for the dmpi trans to CO.

Conclusions

When the carbonyl groups in $\text{M}(\text{CO})_6$ are successively replaced by isocyanide ligands, the following points are observed.

- The metal centers are increasingly deshielded.
- The carbonyl carbons are deshielded by 3 ppm with each substitution. The carbon of a carbonyl group trans to an isocyanide is deshielded by 3 ppm compared to the carbon of a carbonyl group trans to another carbonyl group.
- The CNR carbons, which are shielded upon coordination, are deshielded by 3–4 ppm with each substitution. CNR carbons from an isocyanide trans to a carbonyl group are more shielded than those trans to another isocyanide. The C–NR coupling constants increase from 5 Hz in the free ligand to 16 Hz in the monosubstituted and 14 Hz in the disubstituted complex. No splitting was observed for higher substituted or dmpi complexes.
- The isocyanide nitrogen, which is deshielded upon coordination, becomes slightly more shielded again.
- The CNCR' carbon, which is initially deshielded by 3 ppm, becomes more shielded. Coupling constants around 5 Hz are observed in the free ligands and the monosubstituted complexes. No coupling was observed for dmpi, and the initial deshielding in the molybdenum and tungsten complex was <0.5 ppm.
- The chemical shifts of the R' carbons change only slightly.

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