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Reactions of Organic Isocyanides with the Mixed-Metal Clusters $Cp'_2Mo_2Co_2S_3(CO)_4$ and $Cp'_2Mo_2Co_2S_4(CO)_2$

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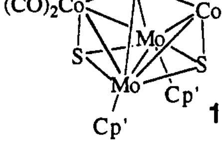
Summary: The bimetallic cluster $Cp'_2Mo_2Co_2S_3(CO)_4$ reacts with tert-butyl or methyl isocyanide to give sequentially the mono-, di-, and trisubstituted clusters $Cp'_2Mo_2Co_2S_3(CO)_{4-x}(L)_x$. The disubstituted derivatives are formed as a mixture of cis and trans isomers that are readily distinguished by their NMR spectra. Color changes and NMR evidence indicate that the adducts $Cp'_2Mo_2Co_2S_3(CO)_{4-x+1}(L)_x$ are formed prior to the loss of CO in the substitution reactions; the reluctance of the adduct with x = 4 to lose CO is invoked to explain the lack of formation of tetrasubstituted derivatives.

The bimetallic sulfido clusters 1 and 2 have shown interesting reactivity, e.g. abstraction of sulfur from organic sulfides,[1,2] a related phenylphosphinidene abstraction from $PhPH_2$,[3] associative carbonyl substitution reactions with organic phosphines,[4,5] and cyclodimerization of acetylenes.[6]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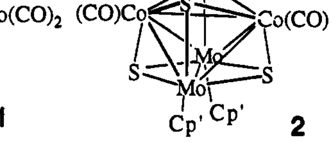
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In this note we report the reactions of 1 and 2 with some organic isocyanides. This study was initiated for several reasons: to confirm the identity of isocyanide adducts observed to form in desulfurization reactions of 1 with isothiocyanates, to compare the substitution chemistry of isocyanides with that of phosphines, and to determine the mode of bonding ($\sigma + \pi$?) of a trisubstituted product obtained from 1 and *tert*-butyl isocyanide that reportedly contained no carbonyl ligands.[7]

Experimental Section

General Considerations. All manipulations and reactions were carried out under a nitrogen atmosphere by use of standard Schlenk-line techniques or by use of a glovebag. Reagent grade solvents were dried and distilled prior to use: toluene, diethyl ether, and tetrahydrofuran from Na/benzophenone; dichloromethane and hexane from CaH_2. $Cp'_2Mo_2Co_2S_3(CO)_4$,[8] $Cp'_2Mo_2Co_2S_4(CO)_2$,[9] and MeNC[10] were prepared by published procedures. All other reagents were purchased from Aldrich Chemical Co. ^1H and ^{13}C NMR data were collected on a Bruker AM-300 or Bruker WM-360 spectrometer. ^{31}P NMR data were collected on a General Electric GN-500 NB spectrometer. IR spectra were obtained on a Nicolet 5-DXB spectrometer. Mass spectra were collected on a Finnegan 4021 quadrupole mass spectrometer. GC-MS spectra were obtained on a VG-70-250-S high-resolution mass spectrometer. Elemental analysis were done by Galbraith Laboratories Inc., Spang Microanalytical Laboratory, or the University of Michigan Microanalysis Laboratory.

Preparation of $Cp'_2Mo_2Co_2S_3(CO)_3(^tBuNC)$. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.100 g, 0.148 mmol) was dissolved in 30 mL of toluene and cooled to −78 °C. ^tBuNC (0.10 mL of a 1.47 M solution in toluene, 0.147 mmol) was added and the solution slowly warmed to room temperature. From approximately −50 to 0 °C, the solution had a red color that turned green-brown as the reaction proceeded at higher temperatures. Elution of the reaction mixture down a 15-cm column of alumina with 1:1 CH_2Cl_2/hexane yielded 0.90 g of brown product (84% yield). ^1H NMR (C_6D_6): δ 5.47 (m, 2H), 5.41 (m, 1H), 5.36 (m, 1H), 5.10 (m, 2H), 5.03 (m, 2H) 2ABCD pattern for Cp*H*, 1.98 (s, 3H, CpC*H*$_3$), 1.91 (s, 3H, CpC*H*$_3$), 0.85 (s, 9H, C(C*H*$_3$)$_3$). IR (toluene): ν(CN) 2110 cm^{-1} (w, br); ν(CO) 1988 (s), 1942 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{23}Co_2Mo_2NO_3S_3$: C, 32.85; H, 3.17; N, 1.92. Found: C, 32.54; H, 3.07; N, 1.73.

Preparation of $Cp'_2Mo_2Co_2S_3(CO)_2(^tBuNC)_2$. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.155 g, 0.23 mmol) was dissolved in 30 mL of toluene and cooled to −78 °C. ^tBuNC (2.10 mL of a 0.26 M solution in toluene, 0.55 mmol) was added and the solution slowly warmed to room temperature. From approximately −50 to 0 °C, a red color corresponding to an intermediate species was observed. The final brown solution was filtered through Celite. Recrystallization of the product from CH_2Cl_2/hexane gave 0.15 g (83% yield) of brown powder. ^1H NMR (C_6D_6): *cis*-$Cp'_2Mo_2Co_2S_3(CO)_2(^tBuNC)_2$ δ 5.65 (t, *J* = 2 Hz), 5.51 (t, *J* = 2 Hz), 5.27 (t, *J* = 2 Hz), 5.16 (t, *J* = 2 Hz) $2A_2B_2$ pattern for Cp*H*, 2.19 (s, 3H, CpC*H*$_3$), 2.04 (s, 3H, CpC*H*$_3$), 0.93 (s, 18H, C(C*H*$_3$)$_3$); *trans*-$Cp'_2Mo_2Co_2S_3(CO)_2(^tBuNC)_2$, δ 5.60 (m, 4H), 5.20 (m, 4H) ABCD pattern for Cp*H*, 2.12 (s, 6H, CpC*H*$_3$), 0.89 (s, 18H, C(C*H*$_3$)$_3$). IR (toluene) of a 3:2 mixture (*trans*/*cis*): ν(CN) 2102 (s), 2072 (m) cm^{-1}; ν(CO) 1988 (w), 1975 (w), 1940 (sh), 1931 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{32}Co_2Mo_2N_2O_2S_3$: C, 36.65; H, 4.10; N, 3.56. Found: C, 36.87; H, 3.96; N, 3.74.

Reaction of $Cp'_2Mo_2Co_2S_3(CO)_4$ with Excess ^tBuNC. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.120 g, 0.18 mmol) was dissolved in 35 mL of toluene, and ^tBuNC (0.75 mL of a 1.47 M solution in toluene, 1.10 mmol) was added at 0 °C. The solution was then heated to 75 °C for 14 h, after which time the IR spectrum showed only bands attributable to the trisubstituted product $Cp'_2Mo_2Co_2S_3(CO)(^tBuNC)_3$. Removal of solvent followed by flash chromatography down an alumina column with 2:1 CH_2Cl_2/hexane as eluant gave 0.13 g (84% yield) of brown $Cp'_2Mo_2Co_2S_3(CO)(^tBuNC)_3$, as confirmed by NMR spectroscopy.

Preparation of $Cp'_2Mo_2Co_2S_3(CO)(MeNC)_3$. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.152 g, 0.225 mmol) was dissolved in 25 mL of toluene and cooled to −78 °C. MeNC (0.25 mL, 4.8 mmol) was added and the solution slowly warmed to room temperature. From ap-

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proximately −50 to 0 °C, the solution had a red color that turned brown as the reaction proceeded at higher temperatures. After it was stirred for an additional 6 h, the brown solution was filtered through Celite. Recrystallization of the product from CH_2Cl_2/hexane gave 0.040 g (25% yield) of brown powder. ^1H NMR (C_6D_6): δ 5.65 (m, 1H), 5.57 (m, 1H), 5.53 (m, 2H), 5.14 (m, 4H) 2ABCD pattern for Cp*H*, 2.35 (s, 3H, CNC*H*$_3$), 2.30 (s, 3H, CNC*H*$_3$), 2.19 (s, 3H, CNC*H*$_3$), 2.18 (s, 6H, CpC*H*$_3$). IR (toluene): 2109 (s, br), 1920 (s) cm^{-1}. The product decomposes on standing; thus, a good elemental analysis could not be obtained. Anal. Calcd for $C_{21}H_{23}Co_2Mo_2N_3OS_3$: C, 35.26; H, 3.24; N, 5.87. Found: C, 29.68; H, 3.31; N, 5.08.

Preparation of $Cp'_2Mo_2Co_2S_4(CO)(^tBuNC)$. $Cp'_2Mo_2Co_2S_4(CO)_2$ (0.103 g, 0.158 mmol) was dissolved in 25 mL of toluene and cooled to −78 °C. A solution of ^{t}BuNC (0.109 mL of 1.47 M in toluene, 0.160 mmol) was added and the solution slowly warmed to room temperature. The solution was then flash-chromatographed through a 1-cm layer of alumina. Recrystallization of the product from CH_2Cl_2/hexane gave 0.075 g (68% yield) of brown compound. ^1H NMR (C_6D_6): δ 5.31 (m, 2H), 5.26 (m, 2H), 5.01 (m, 2H), 4.98 (m, 2H) ABCD pattern for Cp*H*, 1.83 (s, 6H, CpC*H*$_3$), 0.88 (s, 9H, C(C*H*$_3$)$_3$). IR (benzene): ν(CN) 2111 (m) cm^{-1}; ν(CO) 1953 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{23}Co_2Mo_2NOS_4$: C, 30.56; H, 3.28; N, 1.98. Found: C, 31.06; H, 3.21; N, 1.89.

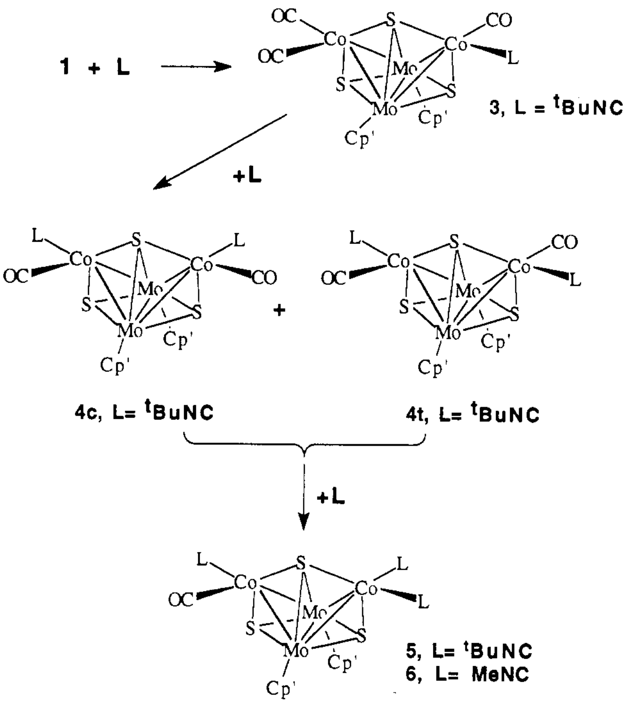
Preparation of $Cp'_2Mo_2Co_2S_4(^tBuNC)_2$. $Cp'_2Mo_2Co_2S_4(CO)_2$ (0.160 g, 0.245 mmol) was dissolved in 25 mL of toluene and cooled to −78 °C. A solution of ^{t}BuNC (2.4 mL of 0.26 M in toluene, 0.62 mmol) was added; the solution was slowly warmed to room temperature and stirred for an additional 3 h, during which time the reaction flask was subjected briefly to vacuum to remove CO, the occasional removal of which appears to be crucial for the reaction to go to completion. The dark green solution was then filtered through Celite, and recrystallization of the product from CH_2Cl_2/hexane gave 0.14 g (75% yield) of dark green rectangular crystals. ^1H NMR (C_6D_6): δ 5.46 (t, *J* = Hz, 4H), 5.26 (t, *J* = 2 Hz, 4H) A_2B_2 pattern for Cp*H*, 2.00 (s, 6H, CpC*H*$_3$), 0.88 (s, 18H, C(C*H*$_3$)$_3$). IR (benzene): ν(CN) 2101 (s), 2071 (ms, br) cm^{-1}. Anal. Calcd for $C_{22}H_{32}Co_2Mo_2N_2S_4$: C, 34.66; H, 4.23; N, 3.67. Found: C, 33.78; H, 4.50; N, 2.44.

Variable-Temperature Reaction of $Cp'_2Mo_2Co_2S_3(CO)_4$ with MeNC. $Cp'_2Mo_2Co_2S_3(CO)_4$ (approximately 20 mg, 0.03 mmol) was dissolved in 0.7 mL of 1:1 $CDCl_3/CCl_4$ in an NMR tube and cooled to −65 °C. MeNC (1.0 μL, 0.02 mmol) was added and the solution mixed by manually shaking the tube. The NMR tube was then placed into the NMR spectromter at −20 °C and the reaction followed as the temperature was raised. At −20 °C, $Cp'_2Mo_2Co_2S_3(CO)_4$ (**1**) and a new compound, $Cp'_2Mo_2Co_2S_3(CO)_4$(MeNC), were observed in a 3:2 ratio. At 5 °C, three compounds, **1**, $Cp'_2Mo_2Co_2S_3(CO)_4$(MeNC), and the CO substitution product $Cp'_2Mo_2Co_2S_3(CO)_3$(MeNC), appear in a 2:2:1 ratio. At room temperature (25 °C) only **1** and $Cp'_2Mo_2Co_2S_3(CO)_3$(MeNC) are present in approximately equal amounts. Some precipitate was observed to form, possibly from a reaction involving the solvent. $Cp'_2Mo_2Co_2S_3(CO)_4$(MeNC): ^1H NMR ($CDCl_3/CCl_4$) δ 5.30 (m, 2H), 5.05 (m, 4H), 5.01 (m, 2H) ABCD pattern for Cp*H*, 3.51 (s, 3H, CNC*H*$_3$), 2.07 (s, 6H, CpC*H*$_3$). $Cp'_2Mo_2Co_2S_3(CO)_3$(MeNC): ^1H NMR ($CDCl_3/CCl_4$): δ 5.59 (m, 4H), 5.24 (m, 4H) 2ABCD pattern for Cp*H*, 3.48 (s, 3H, CNC*H*$_3$), 2.12 (s, 6H, CpC*H*$_3$): IR ($CDCl_3/CCl_4$): ν(CN) 2135 cm^{-1} (m, br), ν(CO) 1994 (s), 1950 (s, br) cm^{-1}.

Results and Discussion

Many of the reactions reported here were followed by spectroscopic techniques (infrared and NMR) or gave products that were characterized spectroscopically. The presence of the methylcyclopentadienyl ligands in $Cp'_2Mo_2Co_2S_3(CO)_4$ (**1**) and $Cp'_2Mo_2Co_2S_4(CO)_2$ (**2**) is especially useful in assigning structures to derivatives of **1** and **2** on the basis of ^1H NMR spectra. Compounds **1** and **2** both have C_{2v} symmetry in which the Cp′ ligands are equivalent. The Cp′ ring protons exhibit an A_2B_2 pattern in the NMR spectrum (actually AA′BB′, but they behave as an A_2B_2 system; i.e., two pseudotriplets are observed), and the Cp′ methyl protons appear as one singlet. Substitution of one carbonyl ligand removes all symmetry; the signals from the Cp′ ligands appear as two ABCD multiplets for the ring protons, and the Cp′ methyl protons give rise to two singlets. Substitution of one carbonyl group on each cobalt atom in **1** can give rise to two isomers: *cis* with C_s symmetry and *trans* with C_2 symmetry. In the former, ring protons appear as two A_2B_2 sets of triplets and the methyl protons as two singlets, while in the latter the corresponding signals appear as one set of ABCD multiplets and one singlet; i.e., the Cp′ groups are equivalent but diastereotopic.

Scheme 1



Compound **1** reacts with 1 equiv of ^{t}BuNC at about −50 °C to give a red solution which becomes brown near 0 °C. The monosubstituted cluster $Cp'_2Mo_2Co_2S_3(CO)_3(^tBuNC)$ (**3**) is obtained as the final product. Compound **3** has no symmetry, but because the anisotropic shielding of the isocyanide ligand is similar to that of the carbonyl groups, only four multiplets are resolved for the two ABCD patterns of the Cp′ ring protons (δ 5.47–5.03); i.e., each set of A/D and B/C pairs have similar chemical shifts. The two singlets for the Cp′ methyl protons appear at 1.98 and 1.91 ppm.

Addition of a second molecule of ^{t}BuNC gives a mixture of the *trans* and *cis* products $Cp'_2Mo_2Co_2S_3(CO)_2(^tBuNC)_2$ (**4t** and **4c**) in a 3:2 ratio. This ratio is also found for these clusters disubstituted with phosphines[5] and is quite reproducible. The isomers are distinguishable by their NMR spectra. For the *trans* isomer, only two multiplets at δ 5.60 and 5.20 are observed for the ABCD patterns of the Cp′ ring protons, again because of the small differences in anisotropic shielding between the isocyanide and carbonyl ligands. The methyl group singlet appears at δ 2.12. The *cis* isomer **4c** shows four peaks (δ 5.57, 5.25, 5.21, 4.68) for the two A_2B_2 patterns and two singlets (δ 2.01, 1.91) for the methyl peaks.

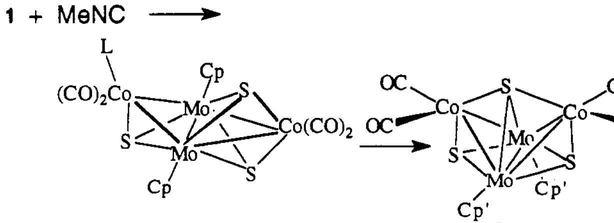
Further reaction with ^{t}BuNC was reported to give a tris(isocyanide) cluster with the proposed formula Cp'_2-

$Mo_2Co_2S_3(^tBuNC)_3$, containing an η^2-μ_3-^tBuNC ligand similar to the η^2-μ_3-alkyne ligand in $Cp'_2Mo_2Co_2S_3(RCCR)(CO)_2$ clusters.[6,7] This formulation was based on the fact that the trisubstituted product showed no resonance attributable to a carbonyl carbon in the ^{13}C spectrum, and the parent ion in a FAB mass spectrum corresponded to the formula as shown. However, the IR spectrum of the tris(isocyanide) cluster contains an absorption at 1918 cm^{-1} that is more consistent with a terminal CO than a η^2-μ_3-bound ^tBuNC ligand, suggesting the formulation $Cp'_2Mo_2Co_2S_3(CO)(^tBuNC)_3$ (**5**), with three terminal isocyanide ligands and a terminal carbonyl ligand.

An analysis of the NMR spectrum also supports the formulation shown for **5**. For this structure, one might expect the chemical shifts of the methyl protons of the *tert*-butyl ligand to follow a pattern based on the mono- and disubstituted derivatives **3** and **4**. The chemical shift for the singlet of the ^tBu group in **3** is 0.85 ppm; addition of a *cis* isocyanide (**4c**) shifts this resonance to 0.93 ppm, while addition of a *trans* isocyanide (**4t**) shifts it to 0.89 ppm. Formation of **5** by the addition of two isocyanides to **3** should shift the singlet to 0.85 + 0.08 + 0.04 = 0.97 ppm. The trisubstituted product has a singlet at 0.96 ppm, a value that agrees well with the predicted chemical shift for the isocyanide on the cobalt atom bearing the carbonyl ligand. Two other singlets due to the *tert*-butyl isocyanide ligands are also observed at 1.12 and 1.07 ppm. These signals can be assigned to the isocyanides on the same Co atom (the difference between these two of 0.05 ppm agrees well with the expected difference of 0.08 − 0.04 = 0.04 ppm). Thus, we conclude that the tris(isocyanide)-substituted cluster **5** retains a carbonyl ligand rather than one $\sigma + \pi$ bound, 4e-donating isocyanide ligand.

To gain additional information on the structure of **5**, the tris(methyl isocyanide) cluster $Cp'_2Mo_2Co_2S_3(CO)(MeNC)_3$ (**6**) was prepared by reaction of **1** with a small excess of methyl isocyanide. While the ν(CN) stretches show the expected shift from an average of 2077 cm^{-1} in **5** to 2109 cm^{-1} in **6**, the ν(CO) absorption only changes by 2 wavenumbers to 1920 cm^{-1}, a clear indication that it is in fact a carbonyl stretch. Like **5**, compound **6** also shows only two ABCD patterns (δ 5.65–5.14) for the Cp′ ring protons. The singlets for the Cp′ methyl protons at 2.18 and 2.19 ppm appear coincidentally with one of the methyl isocyanide singlets, while the singlets for the other two methyl isocyanide ligands appear downfield at 2.35 and 2.30 ppm.

The reaction of **1** with MeNC was followed by NMR spectroscopy. Initially a monoadduct, $Cp'_2Mo_2Co_2S_3(CO)_4(MeNC)$ (**7**), was formed (eq 1). This adduct presumably has the same structure as $Cp'_2Mo_2Co_2S_3(CO)_4(PMe_3)$, i.e. an opened-butterfly structure in which one Co–S bond has been displaced.[4,5] The NMR spectrum of adduct **7** displays an ABCD pattern for the Cp′ ring protons (δ 5.30-5.01) and a singlet for the Cp′ methyl protons (δ 2.07). A singlet at 3.51 ppm is observed for the isocyanide protons. At about 5 °C the monosubstituted product $Cp'_2Mo_2Co_2S_3(CO)_3(MeNC)$ (**8**) begins to form. The NMR spectrum of **8** shows two ABCD patterns for the Cp′ ring protons (δ 5.6-5.2), but the signals of the Cp′ methyl protons are accidentally coincident and only one singlet is seen at 2.12 ppm. The isocyanide protons appear as a singlet at 3.48 ppm. The IR spectrum is similar to that of the ^tBuNC and phosphine monosubstituted clusters—the carbonyl stretches appear at 1994 (s) cm^{-1} and 1950 (s, br) cm^{-1} while the CN stretch appears at 2135 (m, br) cm^{-1}, 25 wavenumbers higher than in the ^tBuNC adduct because of the smaller reduced mass of the methyl group as compared to that of the *tert*-butyl group.

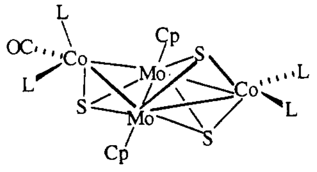


(1)

7, L = MeNC

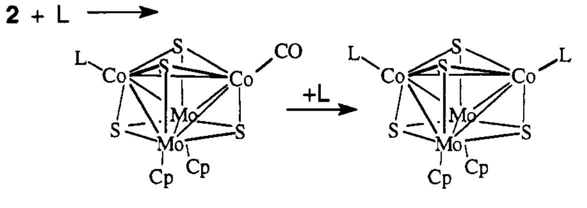
8

Attempts to replace the last carbonyl ligand on **5** or **6** by reaction with an excess of isocyanide at 75 °C were unsuccessful. This behavior can be understood if substitution of all carbonyl groups proceeds by a mechanism that involves the formation of an adduct prior to the actual substitution step (cf. eq 1). Substitution of the fourth CO group would then occur from the adduct **9**. Apparently, loss of the isocyanide ligand in **9** is favored over loss of the carbonyl because of the high electron density on the Co atom.



9, L= RNC

The isocyanide-substituted derivatives of the cubane cluster **2**, prepared from **2** and isocyanides, were identical with the products obtained from the reaction of **1** with ^tBuNCS.[1] Reaction of **2** with 1 or 2 mol equiv of ^tBuNC gave $Cp'_2Mo_2Co_2S_4(CO)(^tBuNC)$ (**10**) and $Cp'_2Mo_2Co_2S_4(^tBuNC)_2$ (**11**), respectively (eq 2). Compound **10** belongs to the C_s point group with the mirror plane perpendicular to the Mo–Mo axis. This complex therefore exhibits one ABCD pattern (δ 5.31–4.98) for the Cp′ ring protons and one singlet at 1.83 ppm for the Cp′ methyl protons. Another singlet is observed at 0.83 ppm for the ^tBu protons. The C–N stretch is observed at 2111 cm^{-1} in the IR spectrum of **10**, and the ν(CO) absorption appears at 1953 cm^{-1}, 20 wavenumbers lower than the average energy for the carbonyl ligands on **2** and similar to the ν(CO) values observed for monosubstituted phosphine derivatives of **2**.[5] The lower value for ν(CO) again suggests that the isocyanide ligands are weaker π-acceptors than CO and that the electronic effects are transmitted from one cobalt atom to the other.



(2)

10, L=^{t}BuNC

11

Compound **11** has the same symmetry as **2** (C_{2v} point group) and thus shows one A_2B_2 pattern (5.46 and 5.11 ppm), one singlet at 2.00 ppm for the Cp′ methyl protons, and one singlet at 0.88 ppm for the ^{t}Bu protons. The IR spectrum shows two C–N stretches at 2101 and 2071 cm^{-1}, down an average of 26 wavenumbers from the C–N stretch in **10**. Again, this is due to the weaker π-acceptor ability of the isocyanide ligands and the transmission of the electronic effects through the cluster.

Comparison of Phosphine and Isocyanide Substitution Reactions. Monodentate phosphines react with **1** to form mono- and disubstituted products analogous to products **3** and **4** (Scheme 1).[5] Trisubstituted clusters similar to **5** or **6** have not been observed. We believe this observation can be explained on the same basis as the failure to form clusters with four isocyanides substituted for the CO ligands in **1** (see above). Phosphines are even poorer π-acceptors than isocyanides, so that once only one CO per Co atom is replaced, preferential loss of phosphine occurs from the intermediate adducts similar to **9**. Under forcing conditions, 2 equiv of the bidentate phosphine dmpe reacts with **1** to form a new type of cluster with one η^2-μ_3-carbonyl ligand and one dmpe bonded to each Co atom.[11]

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