

SUPPORTING INFORMATION

Synthesis of Transition Metal Isocyanide Compounds from Carbonyl Complexes *via* Reaction with Li[Me₃SiNR]

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EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere,¹ with the exception of chromatography that was performed in air. Solvents were purified and degassed by standard procedures. ¹H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ¹H chemical shifts are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta 7.16$ for C₆D₅H).² Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm⁻¹. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). All chemicals were obtained from Aldrich, with the exception of Cr(CO)₆ and W(CO)₆ which were obtained from Strem.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.1).³

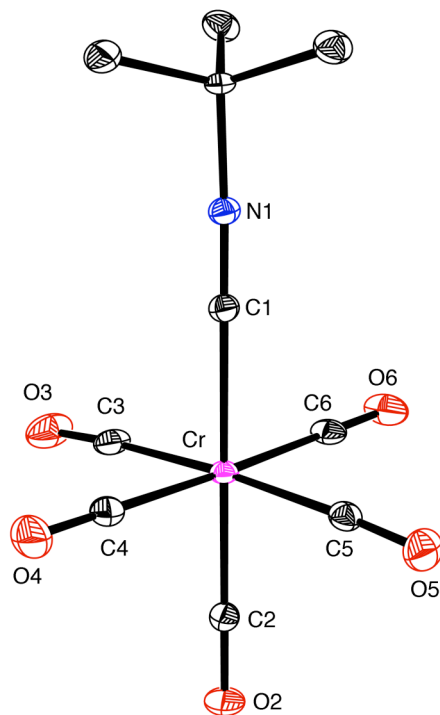
Synthesis of Li[Me₃SiNBu^t]

Li[Me₃SiNBu^t] was prepared by an adaptation of a literature method. A solution of BuⁿLi in hexanes (2.5 M, 3.2 mL, 8.0 mmol) was added dropwise to a solution of Me₃SiN(Bu^t)H (1.32 mL, 6.9 mmol) in Et₂O (*ca.* 10 mL) at -78 °C. The mixture was stirred for 20 minutes at -78 °C, allowed to warm to room temperature, and then stirred for 6 hours. After this period, the solution was concentrated to a volume of *ca.* 1 mL, thereby inducing the deposition of a white precipitate. *n*-Hexane (*ca.* 5 mL) was added and the mixture was filtered and the precipitate was dried *in vacuo* overnight, giving

Li[Me₃SiNBu^t] as a fine white powder (0.94 g, 90 %). ¹H NMR (C₆D₆): 0.2 – 0.4 [bm, 9H, (CH₃)₃SiNBu^t], 1.2 – 1.4 [bm, 9H, Me₃SiNC(CH₃)₃].

Synthesis of Cr(CO)₅(CNBu^t)

A mixture of Cr(CO)₆ (12 mg, 0.05 mmol) and Li[Me₃SiNBu^t] (9 mg, 0.06 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ¹H NMR spectroscopy, thereby indicating the formation of Cr(CO)₅(CNBu^t) after a period of 150 minutes. The resulting mixture was purified by flash column chromatography (silica gel, hexanes) in air to give Cr(CO)₅(CNBu^t) as a microcrystalline solid (9 mg, 60 %) after removal of the solvent *in vacuo*. ¹H NMR (C₆D₆): 0.68 [s, CNC(CH₃)₃]. IR data (hexanes, cm⁻¹): ν_{CN} = 2151 (m); ν_{CO} = 2060 (m), 1958 (s) and 1930 (w).⁴ Crystals suitable for X-ray diffraction were obtained from hexanes.



Molecular Structure of Cr(CO)₅(CNBu^t)

Synthesis of Mo(CO)₅(CNBu^t)

A mixture of Mo(CO)₆ (15 mg, 0.06 mmol) and Li[Me₃SiNBu^t] (9 mg, 0.06 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ¹H NMR spectroscopy, thereby indicating the formation of Mo(CO)₅(CNBu^t) after a period of 30 minutes. The resulting mixture was purified by flash column chromatography (silica gel, hexanes) to give Mo(CO)₅(CNBu^t) as a microcrystalline solid (13 mg, 71 %) after removal of the solvent *in vacuo*. ¹H NMR (C₆D₆): 0.68 [1:1:1 t, ³J_{N-H} = 2, CN(CH₃)₃]. IR data (hexanes, cm⁻¹): ν_{CN} = 2152 (m); ν_{CO} = 2066 (m), 1959 (s) and 1928 (w).⁴

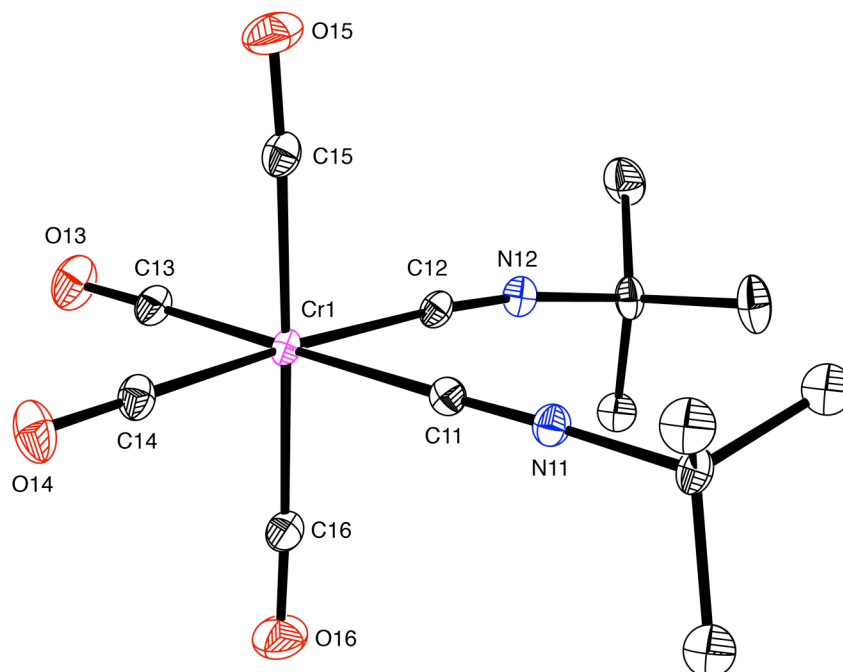
Synthesis of W(CO)₅(CNBu^t)

A mixture of W(CO)₆ (20 mg, 0.06 mmol) and Li[Me₃SiNBu^t] (9 mg, 0.06 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ¹H NMR spectroscopy, thereby indicating the formation of W(CO)₅(CNBu^t) after a period of 30 minutes. The resulting mixture was purified by flash column chromatography (silica gel, hexanes) to give W(CO)₅(CNBu^t) as a microcrystalline solid (13 mg, 56 %) after removal of the solvent *in vacuo*. ¹H NMR (C₆D₆): 0.66 [s, CNC(CH₃)₃]. IR data (hexanes, cm⁻¹): ν_{CN} = 2153 (m); ν_{CO} = 2062 (m), 1954 (s) and 1923 (w).⁴

Synthesis of *cis*-Cr(CO)₄(CNBu^t)₂

A mixture of Cr(CO)₆ (12 mg, 0.05 mmol) and Li[Me₃SiNBu^t] (17 mg, 0.11 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ¹H NMR spectroscopy, thereby indicating the formation of *cis*-Cr(CO)₄(CNBu^t)₂ after a period of 20 hours. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL) and dichloromethane (*ca.* 5 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing colorless crystals of *cis*-

$\text{Cr}(\text{CO})_4(\text{CNBu}^t)_2$ which were isolated by decanting and dried *in vacuo* (6 mg, 33 %). The mother liquor was placed at $-15\text{ }^\circ\text{C}$, thereby depositing a second crop of colorless crystals (7 mg), composed of a *ca.* 1:1 mixture of *cis*- $\text{Cr}(\text{CO})_4(\text{CNBu}^t)_2$ and $\text{Cr}(\text{CO})_5(\text{CNBu}^t)$. $^1\text{H NMR}$ (C_6D_6): 0.85 [s, $\text{CNC}(\text{CH}_3)_3$]. IR data (hexanes, cm^{-1}): $\nu_{\text{CN}} = 2145$ (w) and 2107 (m); $\nu_{\text{CO}} = 2010$ (m) and 1926 (s).⁴ Crystals suitable for X-ray diffraction were obtained from hexanes at $-15\text{ }^\circ\text{C}$.

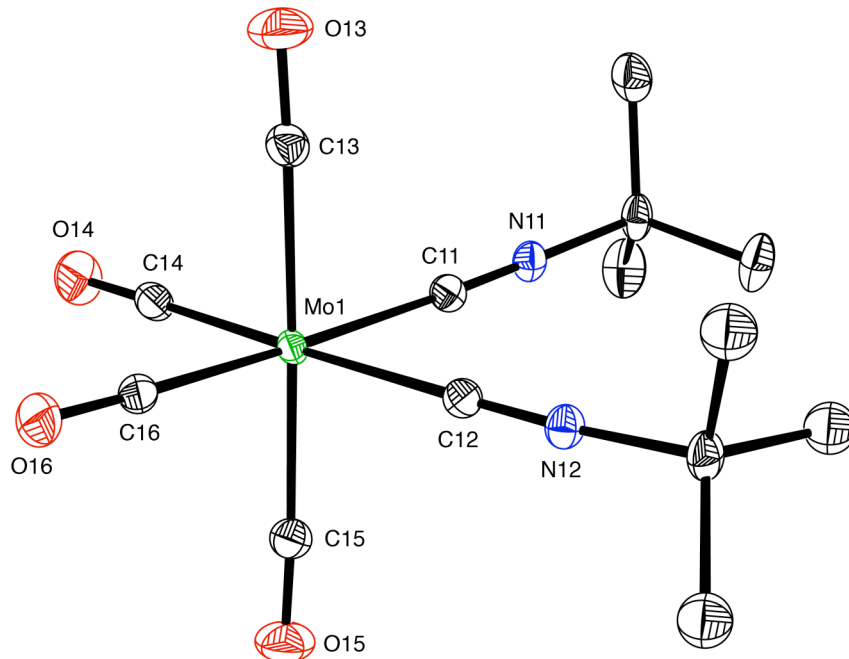


Molecular Structure of cis-Cr(CO)₄(CNBu^t)₂

Synthesis of *cis*-Mo(CO)₄(CNBu^t)₂ (a) A mixture of $\text{Mo}(\text{CO})_6$ (36 mg, 0.14 mmol) and $\text{Li}[\text{Me}_3\text{SiNBu}^t]$ (50 mg, 0.33 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C_6D_6 (0.7 mL). The sample was shaken periodically and monitored by $^1\text{H NMR}$ spectroscopy, thereby indicating the formation of *cis*- $\text{Mo}(\text{CO})_4(\text{CNBu}^t)_2$ after a period of 37 hours at room temperature.⁵ The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at $-15\text{ }^\circ\text{C}$, thereby depositing colorless crystals of *cis*- $\text{Mo}(\text{CO})_4(\text{CNBu}^t)_2$ which were isolated and dried *in vacuo* (41 mg, 81 %). $^1\text{H NMR}$ (C_6D_6): 0.82 [s, $\text{CNC}(\text{CH}_3)_3$]. IR data (hexanes, cm^{-1}): ν_{CN}

= 2146 (w) and 2109 (m); ν_{CO} = 2014 (m) and 1928 (s).⁴ Crystals suitable for X-ray diffraction were obtained from hexanes at $-15\text{ }^{\circ}\text{C}$.

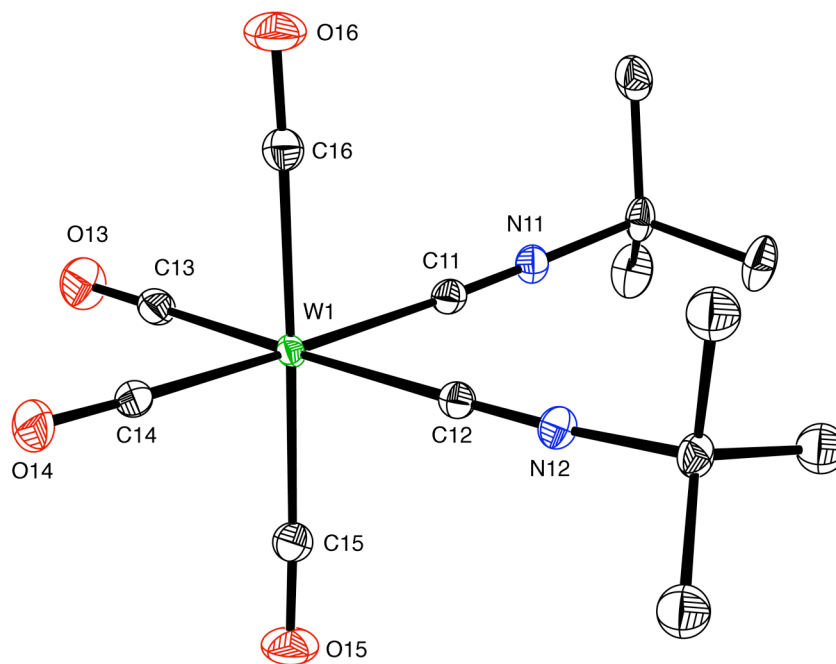
(b) A mixture of $\text{Mo}(\text{CO})_6$ (1.00 g, 3.79 mmol) and $\text{Li}[\text{Me}_3\text{SiNBu}^t]$ (1.26 g, 8.33 mmol) was treated with Et_2O (45 mL) at $-78\text{ }^{\circ}\text{C}$, and then allowed to warm to room temperature with stirring. After a period of 1 day, an additional quantity of $\text{Li}[\text{Me}_3\text{SiNBu}^t]$ (600 mg, 3.97 mmol) was added at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred for an additional 12 hours. After this period, the volatile components were removed *in vacuo*. Hexanes (*ca.* 10 mL) were added and the mixture was filtered through silica gel (*ca.* 25 mL) and eluted with hexanes (*ca.* 350 mL). The filtrate was placed at $-15\text{ }^{\circ}\text{C}$, thereby depositing colorless crystals of *cis*- $\text{Mo}(\text{CO})_4(\text{CNBu}^t)_2$ which were isolated and dried *in vacuo* (506 mg). The mother liquor was then concentrated to *ca.* 50 mL and placed at $-15\text{ }^{\circ}\text{C}$, thereby depositing a second batch of colorless crystals of a 4:1 mixture of *cis*- $\text{Mo}(\text{CO})_4(\text{CNBu}^t)_2$ and $\text{Mo}(\text{CO})_5(\text{CNBu}^t)$ which were isolated and dried *in vacuo* (151 mg).



Molecular Structure of cis-Mo(CO)₄(CNBu^t)₂

Synthesis of *cis*-W(CO)₄(CNBu^t)₂

A mixture of W(CO)₆ (20 mg, 0.06 mmol) and Li[Me₃SiNBu^t] (17 mg, 0.11 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ¹H NMR spectroscopy, thereby indicating the formation of *cis*-W(CO)₄(CNBu^t)₂ after a period of 5 hours. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing colorless crystals of *cis*-W(CO)₄(CNBu^t)₂ which were isolated and dried *in vacuo* (11 mg, 42 %). The mother liquor was placed at -15 °C, thereby depositing a second crop of colorless crystals (6 mg) composed of a *ca.* 1:3 mixture of *cis*-W(CO)₄(CNBu^t)₂ and W(CO)₅(CNBu^t). ¹H NMR (C₆D₆): 0.82 [s, CNC(CH₃)₃]. IR data (hexanes, cm⁻¹): ν_{CN} = 2148 (w) and 2104 (w); ν_{CO} = 2009 (m) and 1922 (s).⁴ Crystals suitable for X-ray diffraction were obtained from hexanes at -15 °C.



Molecular Structure of cis-W(CO)₄(CNBu^t)₂

Synthesis of *fac*-Cr(CO)₃(CNBu^t)₃

A mixture of Cr(CO)₆ (12 mg, 0.05 mmol) and Li[Me₃SiNBu^t] (43 mg, 0.28 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The

sample was heated at 60 °C, shaken periodically, and monitored by ^1H NMR spectroscopy, thereby indicating the formation of *fac*-Cr(CO)₃(CNBu^t)₃ after a period of 69 hours. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing pale yellow crystals of *fac*-Cr(CO)₃(CNBu^t)₃ which were isolated and dried *in vacuo* (3 mg, 14 %). ^1H NMR (C₆D₆): 1.00 [s, CNC(CH₃)₃]. IR data (CH₂Cl₂, cm⁻¹): ν_{CN} = 2150 (w) and 2109 (m); ν_{CO} = 1932 (s) and 1863 (s).⁴

Synthesis of *fac*-Mo(CO)₃(CNBu^t)₃ and *cis*-Mo(CO)₂(CNBu^t)₄

A mixture of Mo(CO)₆ (36 mg, 0.14 mmol) and Li[Me₃SiNBu^t] (70 mg, 0.46 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C₆D₆ (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by ^1H NMR spectroscopy, thereby indicating the formation of *fac*-Mo(CO)₃(CNBu^t)₃ after a period of 3 hours, together with a small amount of *cis*-Mo(CO)₄(CNBu^t)₂. An additional quantity of Li[Me₃SiNBu^t] (70 mg, 0.46 mmol) was added, and the mixture was heated at 60 °C for 1 day. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing pale yellow crystals of *fac*-Mo(CO)₃(CNBu^t)₃ which were isolated and dried *in vacuo* (17 mg, 28 %) contaminated with a small amount (*ca.* 2 %) of *cis*-Mo(CO)₂(CNBu^t)₄. The mother liquor was placed at -15 °C, thereby depositing a second crop of pale yellow crystals (9 mg) composed of a *ca.* 3:1 mixture of *fac*-Mo(CO)₄(CNBu^t)₂ and *cis*-Mo(CO)₂(CNBu^t)₄.

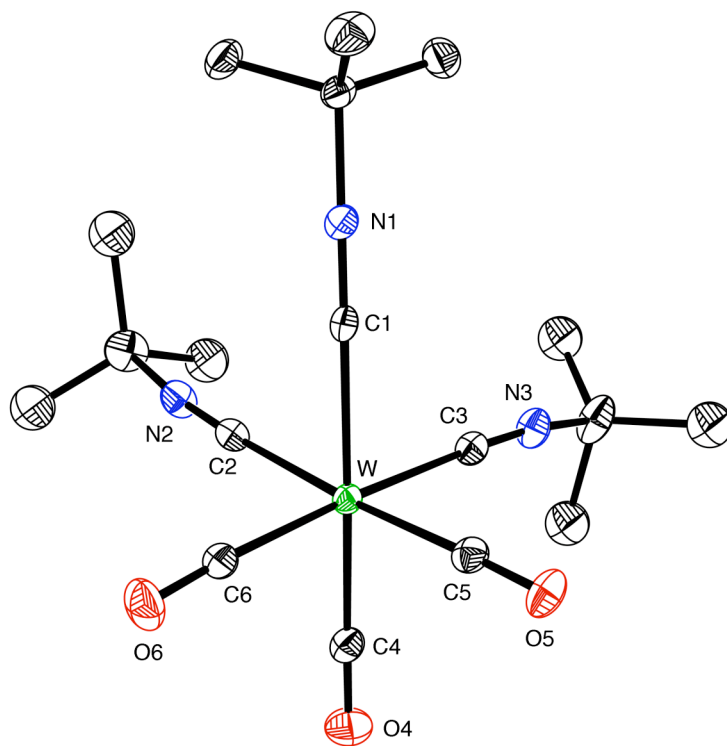
Data for fac-Mo(CO)₃(CNBu^t)₃. ^1H NMR (C₆D₆): 0.95 [s, CNC(CH₃)₃]. IR Data (dichloromethane, cm⁻¹): ν_{CN} = 2154 (w) and 2114 (m); ν_{CO} = 1935 (s) and 1861 (s).⁴

Data for cis-Mo(CO)₂(CNBu^t)₄. ^1H NMR (C₆D₆): 1.04 [s, CNC(CH₃)₃], 1.15 [s, CNC(CH₃)₃].

Synthesis of *fac*-W(CO)₃(CNBu^t)₃

A mixture of W(CO)₆ (20 mg, 0.06 mmol) and Li[Me₃SiNBu^t] (43 mg, 0.28 mmol) placed

in an NMR tube equipped with a J. Young valve was treated with C_6D_6 (0.7 mL). The sample was heated at 60 °C, shaken periodically, and monitored by 1H NMR spectroscopy, thereby indicating the formation of *fac*- $W(CO)_3(CNBu^t)_3$ after a period of 22 hours. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing pale yellow crystals of *fac*- $W(CO)_3(CNBu^t)_3$ which were isolated and dried *in vacuo* (21 mg, 66 %) contaminated with a small amount of *cis*- $W(CO)_2(CNBu^t)_4$ (3 %). The mother liquor was placed at -15 °C, thereby depositing a second batch of pale yellow crystals (3 mg); total yield 24 mg, 80 %. 1H NMR (C_6D_6): 0.95 [s, $CNC(CH_3)_3$]. IR Data (CH_2Cl_2 , cm^{-1}): $\nu_{CN} = 2155$ (w) and 2108 (m); $\nu_{CO} = 1929$ (s) and 1857 (s).⁴ Crystals suitable for X-ray diffraction were obtained from hexanes at -15 °C.

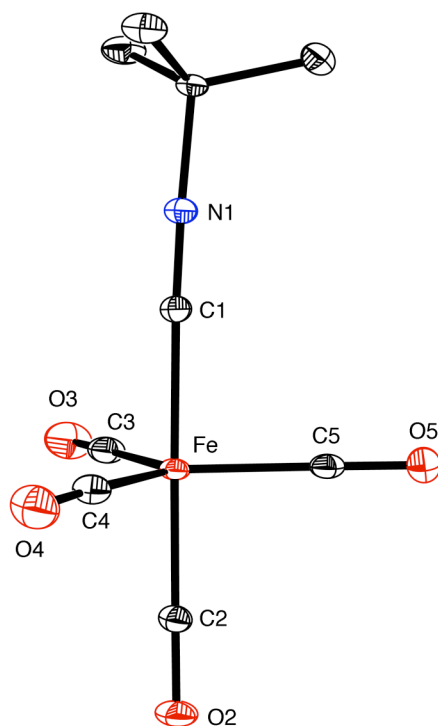


Molecular Structure of fac-W(CO)₃(CNBu^t)₃

Synthesis of *axial*- $Fe(CO)_4(CNBu^t)$

A mixture of $Fe(CO)_5$ (10 μ L, 0.07 mmol) and $Li[Me_3SiNBu^t]$ (11 mg, 0.07 mmol) placed

in an NMR tube equipped with a J. Young valve was treated with C_6D_6 (0.7 mL). The sample was heated at $60\text{ }^\circ\text{C}$ and monitored by ^1H NMR spectroscopy, thereby indicating the formation of *axial*- $Fe(CO)_4(CNBut^t)$ after a period of 20 minutes. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at $-15\text{ }^\circ\text{C}$, thereby depositing colorless crystals of *axial*- $Fe(CO)_4(CNBut^t)$ which were isolated and dried *in vacuo* (9 mg, 48 %) contaminated with a small amount of *trans*- $Fe(CO)_3(CNBut^t)_2$ (< 2 %). ^1H NMR (C_6D_6): 0.66 [s, $CNC(CH_3)_3$]. IR data (hexanes, cm^{-1}): $\nu_{CN} = 2171$ (w); $\nu_{CO} = 2055$ (m), 1993 (m) and 1967 (s).⁶ Crystals suitable for X-ray diffraction were obtained from hexanes at $-15\text{ }^\circ\text{C}$.

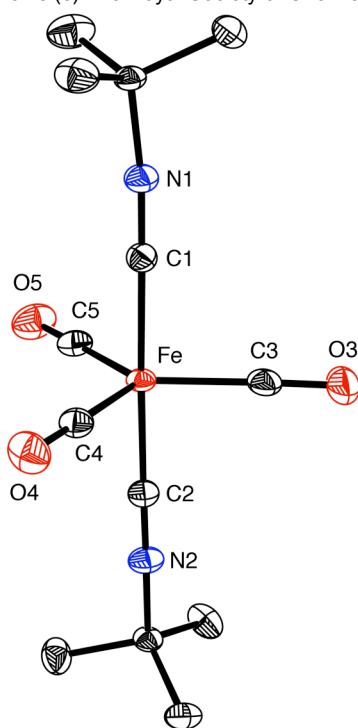


Molecular Structure of $Fe(CO)_4(CNBut^t)$

Synthesis of *trans*- $Fe(CO)_3(CNBut^t)_2$ (a) A mixture of $Fe(CO)_5$ (10 μL , 0.07 mmol) and $Li[Me_3SiNBut^t]$ (25 mg, 0.16 mmol) placed in an NMR tube equipped with a J. Young valve was treated with C_6D_6 (0.7 mL). The sample was heated at $60\text{ }^\circ\text{C}$ and monitored by ^1H NMR spectroscopy, The sample was monitored by ^1H NMR spectroscopy,

thereby indicating the formation of *trans*-Fe(CO)₃(CNBu^t)₂ after a period of 16 hours. The mixture was filtered through silica gel (*ca.* 1 mL) and eluted with hexanes (*ca.* 10 mL) and then dichloromethane (*ca.* 5 mL). The combined filtrate was concentrated to a volume of *ca.* 3 mL and placed at -15 °C, thereby depositing colorless crystals of *trans*-Fe(CO)₃(CNBu^t)₂ which were isolated and dried *in vacuo* (14 mg, 62 %). ¹H NMR (C₆D₆): 0.82 [s, CNC(CH₃)₃]. IR data (hexanes, cm⁻¹): ν_{CN} = 2116 (m); ν_{CO} = 1996 (w) and 1933 (s).⁶ Crystals suitable for X-ray diffraction were obtained from hexanes at -15 °C.⁷

(b) A suspension of Li[Me₃SiNBu^t] (2.00 g, 13.22 mmol) in Et₂O (30 mL) was treated with Fe(CO)₅ (0.812 mL, 1.177 g, 6.01 mmol) at -78 °C. The mixture was stirred and allowed to warm to room temperature. After 16 hours, an additional quantity of Li[Me₃SiNBu^t] (600 mg, 3.97 mmol) was added at -78 °C. The mixture was allowed to warm to room temperature and stirred for 16 hours. After this period, the volatile components were removed *in vacuo*. Hexanes (*ca.* 10 mL) were added and the mixture was filtered through silica gel (*ca.* 25 mL) and eluted with hexanes (*ca.* 200 mL); *caution* – the dry residue on the column may be pyrophoric. The filtrate was placed at -78 °C, thereby depositing pale yellow crystals of *trans*-Fe(CO)₃(CNBu^t)₂ which were isolated and dried *in vacuo* (906 mg, 49 %).

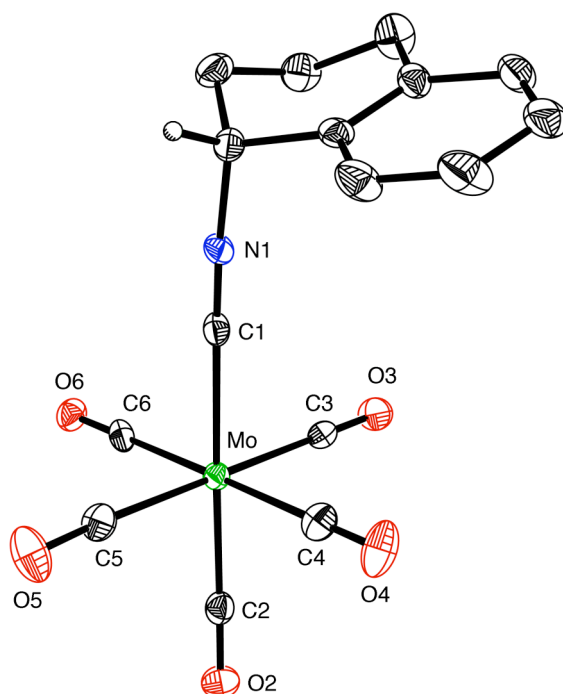


Molecular Structure of Fe(CO)₃(CNBu^t)₂

Synthesis of Mo(CO)₅(CN-1-Np^{H4})

Me₃SiCl (190 μL, 1.5 mmol) was added to a solution of (*R*)-1,2,3,4-tetrahydro-1-naphthylamine (200 μL, 1.36 mmol) in Et₂O (*ca.* 10 mL) and the resulting suspension was stirred for 30 minutes at room temperature, and then treated in a dropwise manner with a solution of BuⁿLi in hexanes (1.6 M, 1.9 mL, 3.0 mmol). The suspension was stirred overnight at room temperature, cooled to -78 °C, and treated with Mo(CO)₆ (180 mg, 0.68 mmol). The suspension was allowed to warm to room temperature and stirred for 6 hours. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into hexanes (*ca.* 20 mL), filtered through silica gel (*ca.* 8 mL) and eluted with hexanes (*ca.* 75 mL) to give Mo(CO)₅(CN-1-Np^{H4}) as a microcrystalline solid (105 mg, 39 %). ¹H NMR (C₆D₆): 1.07 – 1.44 [several multiplets, 4H, C₆H₄C₃H₆CH(NC)], 2.09 – 2.27 [m, 2H C₆H₄C₃H₆CH(NC)], 3.98 [t, ³J_{H-H} = 5, 1H, C₆H₄C₃H₆CH(NC)], 6.69 [m, 1H, C₆H₄C₃H₆CH(NC)], 6.92 [m, 2H, C₆H₄C₃H₆CH(NC)], 7.05 [m, 1H, C₆H₄C₃H₆CH(NC)]. ¹³C{¹H} NMR (C₆D₆): 19.3 [s, 1C, C₆H₄C₃H₆CH(NC)],

28.2 [s, 1C, C₆H₄C₃H₆CH(NC)], 30.2 [s, 1C, C₆H₄C₃H₆CH(NC)], 55.1 [s, 1C, C₆H₄C₃H₆CH(NC)], 126.9 [s, 1C, C₆H₄C₃H₆CH(NC)], 128.0 [s, 1C, C₆H₄C₃H₆CH(NC)], 128.8 [s, 1C, C₆H₄C₃H₆CH(NC)], 129.7 [s, 1C, C₆H₄C₃H₆CH(NC)], 131.6 [s, 1C, C₆H₄C₃H₆CH(NC)], 136.3 [s, 1C, C₆H₄C₃H₆CH(NC)], 152.9 [s, 1C, C₆H₄C₃H₆CH(NC)], 204.4 [s, 4C Mo(CO)₅], 207.1 [s, 1C Mo(CO)₅]. IR data (Hexanes, cm⁻¹): ν_{CN} = 2154 (m); ν_{CO} = 2066 (m), 1960 (s) and 1929 (w). Crystals suitable for X-ray diffraction were obtained from hexanes at -15 °C.



Molecular Structure of Mo(CO)₅(CN-1-Np^{H4})

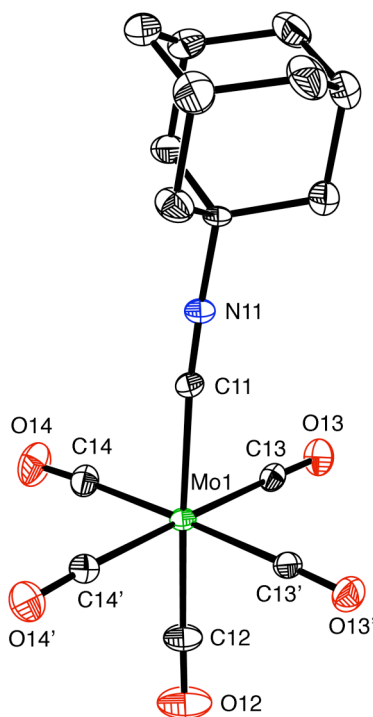
Synthesis of Mo(CO)₅(CN-1-Adamantyl) and *cis*-Mo(CO)₄(CN-1-Adamantyl)₂

Me₃SiCl (100 μL, 0.79 mmol) was added to a suspension of 1-adamantamine, AdNH₂, (70 mg, 0.46 mmol) in Et₂O (*ca.* 10 mL). The suspension was stirred for 30 minutes, cooled to -78 °C, and treated in a dropwise manner with a solution of BuⁿLi in hexanes (2.5 M, 0.40 mL, 1.00 mmol). The resulting solution was allowed to warm to room temperature, thereby depositing a white precipitate. The mixture was stirred for 3 hours at room temperature, cooled to -78 °C, and was treated with Mo(CO)₆ (50 mg, 0.19 mmol). The suspension was allowed to warm to room temperature and was stirred

overnight. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into hexanes (*ca.* 3 mL) and purified by flash chromatography (silica, hexanes, Et₂O gradient). Mo(CO)₅(CN-1-Ad) was the first fraction (24 mg, 32 % based on Mo(CO)₆) and *cis*-Mo(CO)₄(CN-1-Ad)₂ (43 mg, 43 %) was obtained as the second fraction. Crystals of Mo(CO)₅(CN-1-Ad) and Mo(CO)₄(CN-1-Ad)₂ suitable for X-ray diffraction were obtained from hexanes at -15 °C.

Data for Mo(CO)₅(CN-1-Ad)

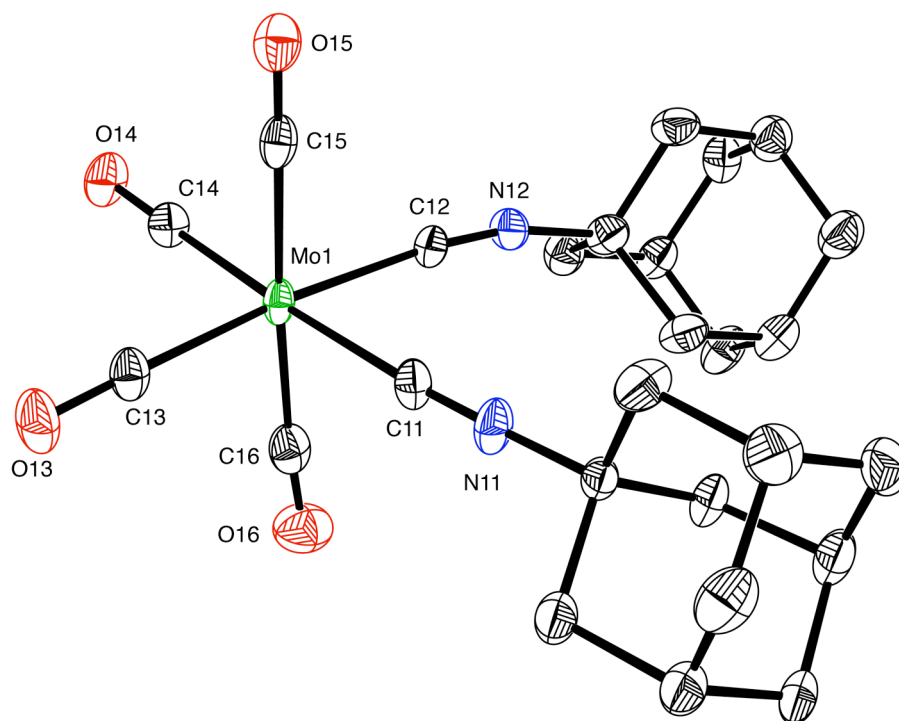
¹H NMR (C₆D₆): 1.12 [m, 6H of Ad], 1.40 [s, 6H of Ad], 1.50 [s, 3H of Ad]. IR data (hexanes, cm⁻¹): ν_{CN} = 2147 (m); ν_{CO} = 2065 (m), 1958 (s), and 1930 (w). Mass spectrum (FAB+): *m/z* = 399.0 {M}⁺.



Molecular Structure of Mo(CO)₅(CN-1-Ad)

Data for cis-Mo(CO)₄(CN-1-Ad)₂

¹H NMR (C₆D₆): 1.18 [m, 6H of Ad], 1.57 [s, 3H of Ad], 1.60 [s, 6H of Ad]. IR data (Et₂O, cm⁻¹): ν_{CN} = 2147 (w) and ν_{CN} = 2115 (m); ν_{CO} = 2016 (m) and 1928 (s). Mass spectrum (FAB+): *m/z* = 532.2 {M}⁺.



Molecular Structure of cis-Mo(CO)₄(CN-1-Ad)₂

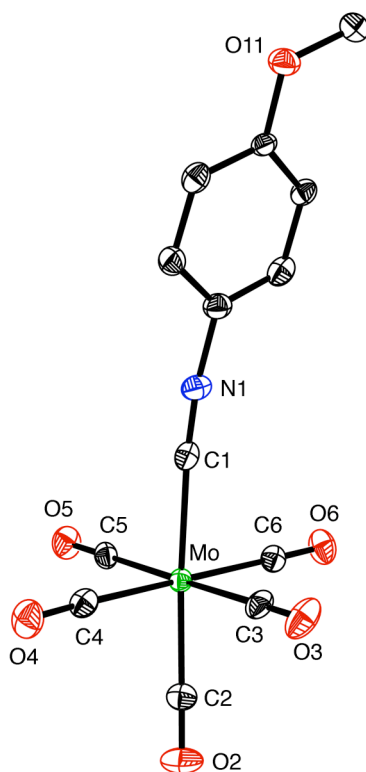
Synthesis of Mo(CO)₅(CN-*p*-C₆H₄Me)

Me₃SiCl (100 μ L, 0.79 mmol) was added to a solution of *p*-MeC₆H₄NH₂ (20 mg, 0.19 mmol) in Et₂O (*ca.* 10 mL) giving a suspension that was stirred for 2 hours, cooled to -78 $^{\circ}$ C, and treated in a dropwise manner with a solution of BuⁿLi in hexanes (2.5 M, 0.17 mL, 0.42 mmol). The resulting solution was allowed to warm to room temperature, thereby depositing a white precipitate. The mixture was stirred for 4 hours at room temperature, cooled to -78 $^{\circ}$ C, and treated with Mo(CO)₆ (50 mg, 0.19 mmol). The mixture was allowed to warm to room temperature and was stirred for 2 days. The volatile components were removed *in vacuo* and the residue obtained was extracted into hexanes (*ca.* 5 mL) and purified by flash column chromatography (silica gel, hexanes), to give Mo(CO)₅(CN-*p*-C₆H₄Me) as a white microcrystalline solid (47 mg, 70 %). ¹H NMR (C₆D₆): 1.79 [s, 3H, CN-*p*-C₆H₄CH₃], 6.46 [s, 4H, CN-*p*-C₆H₄Me]. IR data (hexanes, cm⁻¹): ν_{CN} = 2137 (w); ν_{CO} = 2059 (m), 1965 (s) and 1930 (w). Mass spectrum

(FAB+): $m/z = 355.0 \{M\}^+$.

Synthesis of $\text{Mo}(\text{CO})_5(\text{CN-}p\text{-C}_6\text{H}_4\text{OMe})$

Me_3SiCl (100 μL , 0.79 mmol) was added to a solution of $p\text{-MeOC}_6\text{H}_4\text{NH}_2$ (23 mg, 0.19 mmol) in Et_2O (ca. 10 mL) and stirred for 30 minutes at room temperature. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and treated in a dropwise manner with a solution of Bu^nLi in hexanes (2.5 M, 0.17 mL, 0.42 mmol). The resulting solution was allowed to warm to room temperature, thereby depositing a white precipitate. The mixture was stirred for 2 hours at room temperature, cooled to $-78\text{ }^\circ\text{C}$, and treated with $\text{Mo}(\text{CO})_6$ (50 mg, 0.19 mmol). The mixture was allowed to warm to room temperature and was stirred overnight. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into hexanes (ca. 5 mL) and purified by flash column chromatography (silica gel, hexanes) to give $\text{Mo}(\text{CO})_5(\text{CN-}p\text{-C}_6\text{H}_4\text{OMe})$ as a microcrystalline solid (56 mg, 80 %). $^1\text{H NMR}$ (C_6D_6): 3.03 [s, 3H, $\text{CN-}p\text{-C}_6\text{H}_4\text{OCH}_3$], 6.24 [d, $^3J_{\text{H-H}} = 9\text{ Hz}$, 2H, $\text{CN-}p\text{-C}_6\text{H}_4\text{OCH}_3$], 6.49 [d, $^3J_{\text{H-H}} = 9\text{ Hz}$, 2H, $\text{CN-}p\text{-C}_6\text{H}_4\text{OCH}_3$]. IR data (hexanes, cm^{-1}): $\nu_{\text{CN}} = 2137$ (m); $\nu_{\text{CO}} = 2059$ (m), 1964 (s) and 1942 (w). Mass spectrum (FAB+): $m/z = 371.0 \{M\}^+$. Crystals suitable for X-ray diffraction were obtained from hexanes at $-15\text{ }^\circ\text{C}$.

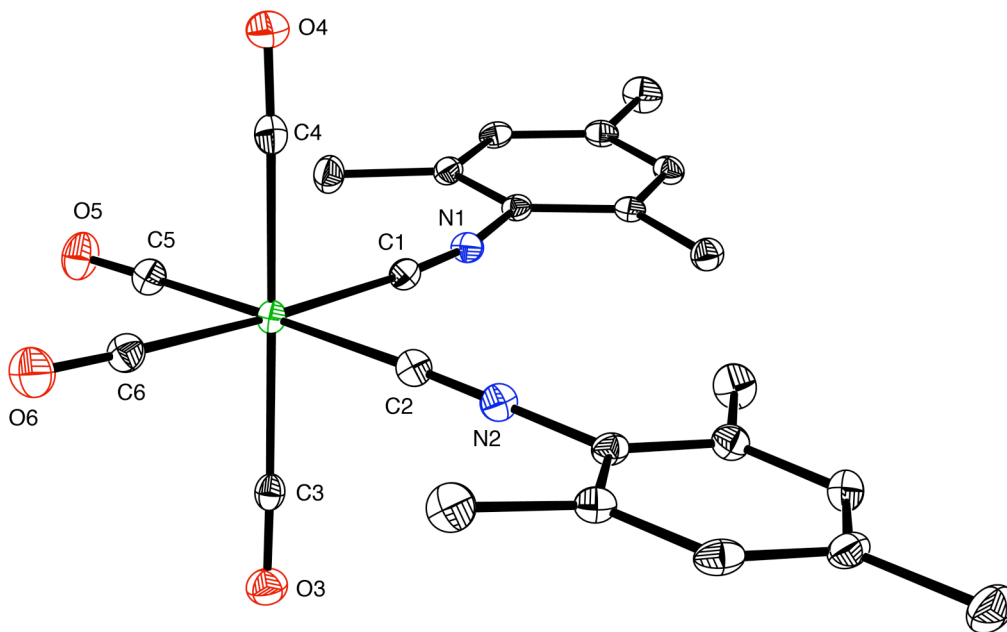


*Molecular Structure of Mo(CO)₅(CN-*p*-C₆H₄OMe)*

Synthesis of *cis*-Mo(CO)₄(CN-2,4,6-C₆H₂Me₃)₂

A solution of BuⁿLi in hexanes (2.5 M, 0.2 mL, 0.5 mmol) was added to a solution of 2,4,6-trimethylaniline (60 μ L, 0.43 mmol) in Et₂O (*ca.* 10 mL). The solution was stirred at room temperature for 2 hours and then cooled to -78 °C, thereby depositing a white precipitate. Me₃SiCl was added dropwise and the mixture was allowed to warm to room temperature, during which period it became a solution and then a suspension. The resulting suspension was allowed to stir for 1 hour at room temperature. After this period, the mixture was treated with a solution of BuⁿLi in hexanes (2.5 M, 0.2 mL, 0.5 mmol). The suspension was stirred for 1 hour, cooled to -78 °C and then treated with Mo(CO)₆ (50 mg, 0.19 mmol). The mixture was allowed to warm to room temperature and then stirred for 2 days at 60 °C. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into hexanes (*ca.* 3 mL) and purified by flash chromatography (silica, hexanes, Et₂O gradient) to give Mo(CO)₄(CN-2,4,6-C₆H₂Me₃)₂ (46 mg, 49 %) as a white microcrystalline solid. ¹H NMR (C₆D₆): 1.90 [s,

3H, CN-2,4,6-C₆H₂(CH₃)₃], 2.09 [s, 6H, CN-2,4,6-C₆H₂(CH₃)₃], 6.39 [s, 2H, CN-2,4,6-C₆H₂Me₃]. IR data (hexanes, cm⁻¹): $\nu_{\text{CN}} = 2131$ (w) and $\nu_{\text{CN}} = 2079$ (m); $\nu_{\text{CO}} = 2013$ (m) and 1940 (s). Mass spectrum (FAB+): $m/z = 500.1$ {M}⁺. Crystals suitable for X-ray diffraction were obtained from hexanes at -15 °C.



Molecular Structure of cis-Mo(CO)₄(CN-2,4,6-C₆H₂Me₃)₂

Table 1. Crystal, intensity collection and refinement data.

	Cr(CO)₅(CNBu^t)	Cr(CO)₄(CNBu^t)₂
lattice	Monoclinic	Monoclinic
formula	C ₁₀ H ₉ CrNO ₅	C ₁₄ H ₁₈ CrN ₂ O ₄
formula weight	275.18	330.30
space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	9.1589(12)	17.0086(16)
<i>b</i> /Å	15.059(2)	11.1264(10)
<i>c</i> /Å	9.3824(12)	18.3223(17)
α /°	90	90
β /°	103.357(2)	101.7850(10)
γ /°	90	90
<i>V</i> /Å ³	1259.1(3)	3394.3(5)
<i>Z</i>	4	8
temperature (K)	125(2)	125(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.452	1.293
μ (Mo K α), mm ⁻¹	0.916	0.689
θ max, deg.	30.49	30.53
no. of data collected	20007	53504
no. of data used	3833	10369
no. of parameters	157	401
R_1 [$I > 2\sigma(I)$]	0.0403	0.0400
wR_2 [$I > 2\sigma(I)$]	0.0811	0.0849
R_1 [all data]	0.0738	0.0746
wR_2 [all data]	0.0926	0.0849
GOF	1.009	1.004

Table 1(cont). Crystal, intensity collection and refinement data.

	Mo(CO)₄(CNBu^t)₂	W(CO)₄(CNBu^t)₂
lattice	Monoclinic	Monoclinic
formula	C ₁₄ H ₁₈ MoN ₂ O ₄	C ₁₄ H ₁₈ WN ₂ O ₄
formula weight	374.24	462.15
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	17.2165(10)	17.109(10)
<i>b</i> /Å	11.2053(7)	11.131(7)
<i>c</i> /Å	18.6121(11)	18.487(11)
α/°	90	90
β/°	101.2930(10)	101.259(8)
γ/°	90	90
<i>V</i> /Å ³	3521.1(4)	3453(4)
<i>Z</i>	8	8
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.412	1.778
μ (Mo Kα), mm ⁻¹	0.759	6.706
θ max, deg.	30.35	32.94
no. of data collected	55011	59772
no. of data used	10593	12348
no. of parameters	401	401
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0393	0.0239
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0696	0.0437
<i>R</i> ₁ [all data]	0.0741	0.0373
<i>wR</i> ₂ [all data]	0.0806	0.0471
GOF	1.001	1.008

Table 1(cont). Crystal, intensity collection and refinement data.

	W(CO)₃(CNBu^t)₃	Fe(CO)₄(CNBu^t)
lattice	Monoclinic	Monoclinic
formula	C ₁₈ H ₂₇ WN ₃ O ₃	C ₉ H ₉ FeNO ₄
formula weight	517.28	251.02
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.2308(12)	8.9045(4)
<i>b</i> /Å	14.955(2)	14.4203(6)
<i>c</i> /Å	16.648(2)	9.0702(4)
α/°	90	90
β/°	94.987(2)	102.7840(10)
γ/°	90	90
<i>V</i> /Å ³	2289.6(5)	1135.79(9)
<i>Z</i>	4	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.501	1.468
μ (Mo Kα), mm ⁻¹	5.063	1.320
θ max, deg.	30.85	32.60
no. of data collected	37064	18983
no. of data used	7183	3954
no. of parameters	227	139
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0390	0.0236
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0711	0.0618
<i>R</i> ₁ [all data]	0.0764	0.0282
<i>wR</i> ₂ [all data]	0.0815	0.0651
GOF	0.992	1.052

Table 1(cont). Crystal, intensity collection and refinement data.

	Fe(CO)₃(CNBu^t)₂	Mo(CO)₅- (CN-<i>p</i>-C₆H₄OMe)
lattice	Orthorhombic	Monoclinic
formula	C ₁₃ H ₁₈ FeN ₂ O ₃	C ₁₃ H ₇ MoNO ₆
formula weight	306.14	369.14
space group	<i>Pbca</i>	<i>P2₁</i>
<i>a</i> /Å	11.6817(9)	10.8089(18)
<i>b</i> /Å	16.0996(13)	5.8009(10)
<i>c</i> /Å	16.4104(13)	11.831(2)
α /°	90	90
β /°	90	107.521(2)
γ /°	90	90
<i>V</i> /Å ³	3086.3(4)	707.4(2)
<i>Z</i>	8	2
temperature (K)	125(2)	125(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.318	1.733
μ (Mo K α), mm ⁻¹	0.982	0.952
θ max, deg.	32.65	32.51
no. of data collected	50292	11852
no. of data used	5476	4735
no. of parameters	178	192
R_1 [$I > 2\sigma(I)$]	0.0226	0.0359
wR_2 [$I > 2\sigma(I)$]	0.0611	0.0751
R_1 [all data]	0.0280	0.0463
wR_2 [all data]	0.0652	0.0789
GOF	1.045	1.005

Table 1(cont). Crystal, intensity collection and refinement data.

	Mo(CO)₄(CN-2,4,6- C₆H₂Me₃)₂	Mo(CO)₅(CN-1-Np^{H₄})
lattice	Triclinic	Orthorhombic
formula	C ₂₄ H ₂₂ MoN ₂ O ₄	C ₁₆ H ₁₁ MoNO ₅
formula weight	498.38	393.20
space group	<i>P</i> -1	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	10.3163(11)	23.215(17)
<i>b</i> /Å	10.5038(11)	12.599(9)
<i>c</i> /Å	11.9238(12)	5.648(4)
α /°	87.101(2)	90
β /°	82.733(2)	90
γ /°	63.7150(10)	90
<i>V</i> /Å ³	1149.1(2)	1652(2)
<i>Z</i>	2	4
temperature (K)	125(2)	200(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.440	1.581
μ (Mo K α), mm ⁻¹	0.602	0.817
θ max, deg.	32.65	28.28
no. of data collected	19899	15546
no. of data used	7821	4090
no. of parameters	286	209
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0367	0.0411
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0839	0.0674
<i>R</i> ₁ [all data]	0.0518	0.1018
<i>wR</i> ₂ [all data]	0.0907	0.0912
GOF	1.027	1.037

Table 1(cont). Crystal, intensity collection and refinement data.

	Mo(CO)₅(CN-1-Ad)	Mo(CO)₄(CN-1-A)₂
lattice	Orthorhombic	Triclinic
formula	C ₁₆ H ₁₄ MoNO ₅	C ₂₆ H ₃₀ MoN ₂ O ₄
formula weight	396.22	530.46
space group	<i>Pnma</i>	<i>P-1</i>
<i>a</i> /Å	23.3043(9)	12.833(8)
<i>b</i> /Å	10.5340(4)	13.248(9)
<i>c</i> /Å	14.0154(5)	16.906(11)
α /°	90	94.485(10)
β /°	90	107.173(10)
γ /°	90	112.316(10)
<i>V</i> /Å ³	3440.6(2)	2481(3)
<i>Z</i>	8	4
temperature (K)	200(2)	200(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.530	1.420
μ (Mo K α), mm ⁻¹	0.785	0.562
θ max, deg.	30.51	25.35
no. of data collected	53927	27609
no. of data used	5510	9079
no. of parameters	235	959
R_1 [$I > 2\sigma(I)$]	0.0349	0.0580
wR_2 [$I > 2\sigma(I)$]	0.0911	0.0971
R_1 [all data]	0.0454	0.1567
wR_2 [all data]	0.0984	0.1273
GOF	1.053	0.956

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