D-7500 Karlsruhe). Hydrogen (Linde high purity grade 99.999%) and α-(Acetylamino)cinnamic acid (Fluka) were used as purchased. α-(Acetylamino)cinnamic acid methyl ester,[7] $[(COD)RhCl]_2$,[17] $[(COD)_2Rh]BF_4$,[18] (P*S*,3*R*,4*R*,P′*S*)-, (P*R*,3*R*,4*R*,P′*R*)-, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine[1] were prepared according to reported procedures.

Preparation of the Catalysts. To a solution of 0.61 mmol of the respective carefully dried 3,4-bis(phosphino)pyrrolidine in 15 mL of CH_2Cl_2 were added 0.25 g (0.60 mmol) of $[(COD)_2Rh]BF_4$. The resulting yellow-red solution was filtered over Kieselguhr. The solvent was removed and the residue dried under vacuum.

[(P*R*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (2): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1385 (P—CH_2Ph), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 26.85 (d, $J_{P,Rh}$ = 144 Hz, first rotamer,[19] the two different P atoms are not resolved), 26.55 (d, $J_{P,Rh}$ = 143 Hz, second rotamer). Anal. Calcd for $C_{43}H_{51}BF_4NO_2P_2Rh{\cdot}CH_2Cl_2$: C, 55.60; H, 5.62; N, 1.47. Found: C, 55.80; H, 5.98; N, 1.43.

[(P*S*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (3): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 21.11 (d, $J_{Rh,P}$ = 151.6 Hz, no rotamers resolved).

[(P*R*,3*R*,4*R*,P′*R*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (4): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 18.00 (d, $J_{Rh,P}$ = 147.8 Hz, first rotamer), 17.70 (d, $J_{Rh,P}$ = 147.6 Hz, second rotamer).

[(P*R*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (5): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 23.75, 20.48 (ABX spin system, $J_{P(a),P(b)}$ = 12.4 Hz, $J_{P(a),Rh}$ = 143.4 Hz, $J_{P(b),Rh}$ = 153.9 Hz, first rotamer), 24.07, 20.17 (ABX spin system, $J_{P(a),P(b)}$ = 12.4 Hz, $J_{P(a),Rh}$ = 143.9 Hz, $J_{P(b),Rh}$ = 153.4 Hz, second rotamer). Anal. Calcd for $C_{31}H_{43}BF_4NO_2P_2Rh{\cdot}1.5CH_2Cl_2$: C, 46.43; H, 5.52; N, 1.67. Found: C, 46.70; H, 5.98; N, 1.85.

Catalytic Hydrogenations. The substrate, as a catalyst either complexes **1**–**5** or $[(COD)_2Rh]BF_4$ or $[(COD)RhCl]_2$, and the ligand were weighed out, placed in the autoclave, and dissolved in 30–50 mL of methanol. The autoclave was closed, thoroughly evacuated, and flushed at least three times with 1 atm of argon to ensure a completely oxygen-free environment. The evacuated autoclave was filled with hydrogen and the reaction started with rapid stirring. At 1 and 2 atm the pressure was kept constant and the hydrogen uptake was measured. At higher pressures the volume was kept constant and the pressure drop (typically 10%) was measured. With α-(acetylamino)cinnamic acid as the substrate the workup was as reported.[12] With the ester as the substrate the reaction mixture was evaporated and the residue was chromatographed in diethyl ether over silica. In all cases the quantitative hydrogenation was confirmed with a ^1H NMR spectrum. The optical yield was determined by comparison with the specific rotations of the pure enantiomers [(*S*)-*N*-acetylphenylalanine, $[\alpha]_D^{22}$ = 47.4 (*c* = 1.0, 95% EtOH);[20] (*S*)-*N*-acetylphenylalanine methyl ester, $[\alpha]_D^{22}$ = 15.9 (*c* = 2.0, CH_3OH)[21]].

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Reactions of Dianionic Carbonylmetalates with Heteroallenes: Reduction of Carbonyl Sulfide, Isothiocyanates, Isocyanates, and Carbodiimides by Group 6 and 8 Carbonylmetalates[1]

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Dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes $X{=}C{=}Y$ to coordinated $C{\equiv}X$ ligands, provided X is a first-row element (N or O) which can form a strong triple bond with C. Thus $Na_2[M(CO)_4]$ (M = Fe, Ru) and $Na_2[M(CO)_5]$ (M = Cr, W) react readily with COS to give $[M(CO)_5]$ (M = Fe, Ru) and $[M(CO)_6]$ (M = Cr, W) in good yield, as established by absorbance mode IR for Fe and W and by isolation of the known derivatives $[M(CO)_4I_2]$ (M = Fe, Ru) and $[N(n\text{-}Bu)_4][M(CO)_5Br]$ (M = Cr, W), while CS_2 does not give thiocarbonyl complexes with $Na_2[W(CO)_5]$ or $Na_2[Fe(CO)_4]$. It is suggested on the basis of IR and stoichiometry that the COS reductions are reductive disproportionations leading to thiocarbonate formation. Isothiocyanates RNCS (R = Ph, Me) give moderate yields of the corresponding isonitrile complexes $[M(CO)_4(CNR)]$ with $Na_2[Fe(CO)_4]$, but not with $Na_2[Ru(CO)_4]$. A similar reaction of PhNCS with $Na_2[Cr(CO)_5]$ gives low yields of $[Cr(CO)_5(CNPh)]$, but $[W(CO)_5(CNPh)]$ can only be isolated after addition of oxalyl chloride to the intermediate isothiocyanate complex. Reduction of PhNCO with $Na_2[W(CO)_5]$ leads to 84% and 5% solution yields of $[W(CO)_6]$ and $[W(CO)_5(CNPh)]$, respectively, consistent with control of the reduction of unsymmetrical heteroallenes by the relative triple bond strengths in the product $C{\equiv}X$ ligands ($C{\equiv}O > C{\equiv}N > C{\equiv}S$).

We have previously reported that dianionic carbonylmetalates characteristically induce reductive disproportionation of carbon dioxide to coordinated carbon monoxide and carbonate,[3] and we have also established, in the

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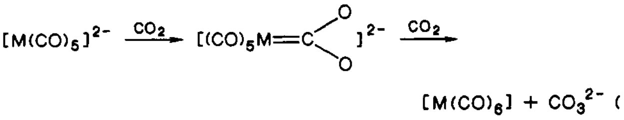
case of the pentacarbonyl dianions of the group 6 metals, that these reactions proceed through intermediate η^1-CO_2 complexes (eq 1).[3] We suggested that the facility of these


$$[M(CO)_5]^{2-} \xrightarrow{CO_2} [(CO)_5M{=}C(O)(O)]^{2-} \xrightarrow{CO_2} [M(CO)_6] + CO_3^{2-} \quad (1)$$

reactions reflected the enhanced nucleophilicity of the CO_2 oxygen atoms as a result of the transfer of electron density from the transition-metal center onto the oxygen atoms of the coordianted CO_2, and it is not unreasonable that η^1-coordination of other heteroallenes[4] to dianionic carbonylmetalates could result in similar activation of the heteroatoms and lead to reductive disproportionation, particularly since the reactions of heteroallenes with some neutral electron-rich transition-metal complexes have been reported to result in examples of the general reductive disproportionation reaction shown in eq 2.

$$2e^- + 2X{=}C{=}Y \rightarrow X{\equiv}C + CXY_2^{2-} \quad (2)$$

Heteroallene reductive disproportionation is probably best established for isothiocyanates (RN=C=S), particularly with complexes of the platinum group metals, several of which have been reported to give complexes containing both isonitrile and dithiocarbonimidato ($S_2C{=}NR$) ligands following treatment with isothiocyanates.[5-7] It has also been reported that carbon disulfide undergoes reductive disproportionation with Rh(I) complexes[8] and that carbonyl sulfide undergoes reductive disproportionation with $[V(\eta\text{-}C_5H_5)_2]$[9] and with zerovalent complexes of the iron[10] and nickel[11] triads. Urylene (NR(O)C=NR) complexes have been formed from isocyanates (RN=C=O),[12-15] and there are two systems in which a reaction with a carbodiimide leads to products indicative of reductive disproportionation.[16,17]

The possibility that they might promote facile reductive disproportionation has led us to examine the reactions of dianionic carbonylmetalates of the group 6 and 8 metals with a range of heteroallenes, with the objective of gaining a better general understanding of heteroallene disproportion by determining its facility with a variety of substrates and by determining the preferred direction of reduction of unsymmetrical heteroallenes such as isocyanates and isothiocyanates.

Previous studies of the reactions of heteroallenes other than CO_2 with dianionic transition-metal complexes are limited. Fehlhammer has reported that $Na_2[Cr(CO)_5]$ reacts with CS_2 in the presence of $[Pt(PPh_3)_2Cl_2]$ to give a trithiocarbonate-bridged binuclear complex $[(CO)_5Cr(\mu\text{-}SCS_2)Pt(PPh_3)_2]$ in moderate yield[18] and more recently that sulfide can be abstracted by phosgene from the intermediate 1:1 adduct of PhNCS with $[Cr(CO)_5]^{2-}$ to give the isonitrile complex $[Cr(CO)_5(CNPh)]$.[19] Similar reactions of the chromium pentacarbonyl dianion with carbodiimides RN=C=NR (R = C_6H_{11}, Ph) have been reported to give 1:1 adducts which could also be converted to isonitrile complexes by treatment with phosgene, or to diaminocarbenes by addition of HCl.[20,21]

Experimental Section

General Data. Solvents and Reagents. All manipulations were conducted under prepurified dinitrogen or argon by means of standard Schlenk techniques unless otherwise indicated. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and distilled under N_2 from sodium benzophenone ketyl. Toluene was dried over sodium wire and distilled under N_2 from powdered CaH_2. *n*-Pentane was stirred over concentrated H_2SO_4 for 24 h, neutralized over anhydrous K_2CO_3 for 12 h, and distilled under N_2 from $Li[AlH_4]$. Dichloromethane was distilled from powdered CaH_2. All solvents were degassed immediately before use.

The following commercial reagents were used as received: $[Cr(CO)_6]$ (Pressure), $[W(CO)_6]$ (Pressure Chemical), NMe_3 (Matheson Gas Products), $[Ru_3(CO)_{12}]$ (Strem Chemicals), naphthalene (MCB Reagents or Baker), I_2 (Mallinckrodt), $[NBu_4]Br$ (Alfa), $Me_3N\cdot 2H_2O$ (Aldrich), oxalyl chloride (Fluka), PhNCS (Alfa), PhNCO (Aldrich), and MeNCO (Aldrich). Sodium (Fisher) and potassium (Baker) were freshly cut under N_2, and lithium metal, alloyed with 1% sodium (Alfa-Ventron or Cerac), was freshly cut under sodium dried mineral oil and handled under argon. Liquid NH_3 was freshly distilled from sodium before use. CS_2 (Fisher) was dried over 3-Å molecular sieves, and COS (Matheson Gas Products) was passed through a 40-cm column packed with a 1:1 mixture of anhydrous $CaCl_2$ and activated 3-Å molecular sieves (Linde). CH_3NCS (Aldrich) was distilled from P_2S_5, and PhNCNPh was prepared according to the literature.[22] Collman's reagent ($Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane, 99.5%) was purchased from Alfa-Ventron and rinsed with THF immediately before use to remove trace quantities of $Na[HFe(CO)_4]$. Solutions of alkali-metal salts of the pentacarbonyl dianions of the group 6 metals ($M'_2[M(CO)_5]$) were prepared in THF by naphthalenide reduction of the corresponding amine complexes $[M(CO)_5(NMe_3)]$ as previously reported.[23] $Na_2[Ru(CO)_4]$ was prepared by Na reduction of $[Ru_3(CO)_{12}]$ in NH_3, as reported in the literature.[24]

Infrared spectra were recorded on a Perkin-Elmer Model 457A or Model 683 spectrophotometer. Solution samples were analyzed in gas-tight demountable NaCl cells (0.1 mm path length) sealed

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with 5-mm rubber serum caps. Nujol mulls were analyzed as thin films between NaCl plates. Spectra were calibrated relative to the sharp 1601 cm^{-1} band of polystyrene. Mass spectra were recorded on an AEI MS-9 double-focusing spectrometer.

Reaction of $Na_2[Fe(CO)_4]\cdot 1.5p$-Dioxane with Excess COS and Conversion of the Product $[Fe(CO)_5]$ to *cis*-$[Fe(CO)_4I_2]$. Dried COS (50.0 mL, 0.124 g, 2.07 mmol) was syringed over 1 min into a vigorously stirred tan suspension of $Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane (0.322 g, 0.93 mmol) in 26.0 mL of THF at ambient temperature. After 10 min the reaction mixture was allowed to settle and the principal ν_{CO} absorptions in IR spectra of the pale yellow solution were those of $[Fe(CO)_5]$ at 2023 (s) and 1992 (vs) cm^{-1}. Absorbance mode spectra indicated an effective $[Fe(CO)_5]$ concentration of 0.026 M (based on $\epsilon = 3500\ M^{-1}\ cm^{-1}$ for the 1992 cm^{-1} band), corresponding to a 73% yield. The solution was filtered into a vessel containing I_2 (0.230 g, 0.91 mmol). The solution changed to a deep red-brown color with gas evolution. Solution IR spectra after 12 min showed quantitative consumption of $[Fe(CO)_5]$ and the appearance of ν_{CO} absorptions consistent with formation of *cis*-$[Fe(CO)_4I_2]$.[25] Solvent was removed under reduced pressure, and the microcrystalline red-black product was maintained at 0.05 mmHg for 2 h. Extraction with 20 mL of toluene, filtration, and solvent removal in vacuo provided microcrystalline red-black *cis*-$[Fe(CO)_4I_2]$ (0.281 g, 0.67 mmol ≡ 72% relative to $Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane). IR (toluene): 2138 (m), 2092 (s), 2072 (m) cm^{-1}. The initial THF-insoluble solid was dried under reduced pressure to yield a tan powder (0.091 g).

Reaction of $Na_2[Ru(CO)_4]$ with Excess COS and Conversion of the Product $[Ru(CO)_5]$ to *cis*-$[Ru(CO)_4I_2]$. Dried COS (50.0 mL, 0.126 g, 2.10 mmol) was syringed in the dark into a rapidly stirred yellow-tan suspension of $Na_2[Ru(CO)_4]$ (0.238 g, 0.92 mmol) in 30 mL of THF at 4 °C over 1 min. After 10 min the flocculent pale yellow precipitate was permitted to settle. Solution IR spectra showed the appearance of strong ν_{CO} absorptions at 2045 and 1994 cm^{-1} consistent with the presence of $[Ru(CO)_5]$.[25] The THF solution was filtered into a vessel containing I_2 (0.223 g, 0.88 mmol) at 4 °C. After 30 min at 4 °C and 25 min at room temperature, the stirred mixture gave a clear light orange solution. Solution IR spectra contained ν_{CO} absorptions consistent with formation of *cis*-$[Ru(CO)_4I_2]$.[26] Removal of solvent under reduced pressure gave a dark orange-red residue from which excess I_2 was sublimed (60 °C, 0.05 mmHg) over 2 h, to leave a bright orange-yellow solid. Extraction with 30 mL of 2:1 CH_2Cl_2/THF, filtration, and solvent removal in vacuo yielded powdery golden yellow *cis*-$[Ru(CO)_4I_2]$ (0.307 g, 0.66 mmol ≡ 72% based on $Na_2[Ru(CO)_4]$). IR (CH_2Cl_2): 2171 (m), 2118 (s), 2080 (m), 2056 (w) cm^{-1}. The original THF-insoluble residue was dried under reduced pressure to give 0.108 g of orange-brown solid. Nujol mull IR spectra of this were dominated by broad absorptions at 1450–1400 and ca. 900 cm^{-1}.

Reaction of $Na_2[Cr(CO)_5]$ with Excess COS and Conversion of the Product $[Cr(CO)_6]$ to $[N(n\text{-}Bu)_4][Cr(CO)_5Br]$. Dried COS (55 mL, 0.136 g, 2.26 mmol) was syringed into a 0.044 M solution of $Na_2[Cr(CO)_5]$ in THF (23.6 mL, 1.04 mmol) at −78 °C over 1 min. The mixture immediately bleached and then gave a milky yellow suspension that precipitated as the mixture was warmed to room temperature. IR spectra of the filtered solution indicated quantitative consumption of $Na_2[Cr(CO)_5]$ and the formation of $[Cr(CO)_6]$ (ν_{CO} = 1978 (s) cm^{-1}). Weaker bands were also observed at 1920 (m) and 1870 (sh) cm^{-1}, consistent with the presence of some $Na[Cr(CO)_5SC(O)H]$.[27] The precipitate was washed with 2 × 5 mL of THF. Solid $[N(n\text{-}Bu)_4]Br$ (0.335 g, 1.04 mmol) and $Me_3NO\cdot 2H_2O$ (0.115 g, 1.04 mmol) were added sequentially to the stirred filtrate. The added solid dissolved within 3.5 h. IR spectra of the golden yellow filtered solution indicated complete consumption of $[Cr(CO)_6]$. After solvent removal in vacuo the product was rinsed with 4 × 20 mL of *n*-pentane and dried under reduced pressure to give $[N(n\text{-}Bu)_4][Cr(CO)_5Br]$[28] as a powdery mustard-yellow solid (0.435 g, 0.85 mmol ≡ 82% relative to $[Cr(CO)_5(NMe_3)]$). IR (THF): 2059 (w), 1963 (sh), 1918 (vs), 1860 (ms) cm^{-1}. The original THF-insoluble precipitate was dried in vacuo over 20 min to provide 0.12 g of greenish tan solid.

Reaction of $Na_2[W(CO)_5]$ with Excess COS and Conversion of the Product $[W(CO)_6]$ to $[N(n\text{-}Bu)_4][W(CO)_5Br]$. Gaseous COS (40.0 mL, 0.099 g, 1.65 mmol) was syringed into a vigorously stirred 0.020 M solution of $Na_2[W(CO)_5]$ in THF (39.0 mL, 0.78 mmol) at −78 °C over 2 min. The reaction mixture rapidly bleached to a clear light yellow and then clouded. The suspension was warmed to room temperature, and dry N_2 was briefly (2 min) bubbled through the mixture (this facilitated precipitation of a flocculent pale yellow solid). THF (35 mL) was added, and the precipitate was permitted to settle. IR spectra of the clear, light yellow filtered solution indicated complete consumption of $Na_2[W(CO)_5]$ and the formation of $[W(CO)_6]$. Weaker bands at 1910 (m) and 1858 (w) cm^{-1} were also observed, consistent with the presence of some $Na[W(CO)_5SC(O)H]$.[29] Absorbance mode IR spectra of a 1.0-mL aliquot of the supernatant indicated an 8.02 M concentration of $[W(CO)_6]$ (based on $\epsilon = 14\,400\ M^{-1}\ cm^{-1}$ for the 1973 cm^{-1} band), corresponding to a $[W(CO)_6]$ yield of 0.59 mmol, or 74% relative to $[W(CO)_5(NMe_3)]$. H_2O (100 mL) was added to the filtered solution, and the yellow emulsion separated by addition of 40 mL of Et_2O and 0.50 g of NaCl. The pale yellow organic phase was decanted onto 2.50 g of anhydrous $CaCl_2$ and the aqueous phase extracted with a further 4 × 10 mL of Et_2O. After 25 min the solution was filtered and $[N(n\text{-}Bu)_4]Br$ (0.187 g, 0.58 mmol) and $Me_3NO\cdot 2H_2O$ (0.064 g, 0.58 mmol) were added sequentially. After 21.5 h at room temperature the stirred solution was a clear golden yellow. Solvent removal under reduced pressure followed by 3 × 35 mL rinses with 1:1 Et_2O/pentane afforded an amorphous yellow ochre solid. Extraction into 20 mL of CH_2Cl_2, filtration, and solvent removal in vacuo provided flaky yellow $[N(n\text{-}Bu)_4][W(CO)_5Br]$[30] (0.292 g, 0.45 mmol ≡ 57% relative to $[W(CO)_5NMe_3]$). IR (CH_2Cl_2): 2070 (w), 1964 (sh), 1918 (vs), 1847 (m) cm^{-1}. The original THF-insoluble precipitate was dried under reduced pressure to give 0.075 g of powdery buff solid. IR (Nujol): ca. 1440 (ms, vbr), 1264 (m), 904 (ms, br) cm^{-1}.

The initially formed $[W(CO)_6]$ was isolated from a similar experiment in which dry COS was added at 200 mL/min to a rapidly stirred 0.062 M solution of $Na_2[W(CO)_5]$ (21.3 mL, 1.32 mmol) at −78 °C for 30 s. The reaction mixture immediately bleached to pale yellow and was stirred for a further 5 min. After the mixture had settled for 25 min, the finely divided, yellow-white precipitate was collected by filtration at −78 °C. The wet solid was washed with H_2O (4 × 5 mL) at room temperature and then with 5 mL of Et_2O at −60 °C and then dried under a slow stream of air. This gave bright white $[W(CO)_6]$ (0.282 g, 0.80 mmol ≡ 61% relative to $[W(CO)_5(NMe_3)]$). IR (Nujol): 1980 cm^{-1}.

Reaction of $Na_2[Fe(CO)_4]\cdot 1.5p$-Dioxane with PhNCS and Isolation of $[Fe(CO)_4(CNC_6H_5)]$. Neat PhNCS (0.77 mL, 0.87 g, 6.41 mmol) was injected into a rapidly stirred suspension of $Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane (1.108 g, 3.20 mmol) in 20 mL of THF at 4 °C. The initial golden amber suspension gradually darkened to an opaque dark red color over 1 h. After the mixture was permitted to settle, IR spectra of the deep red supernant contained the following absorptions; 2174 (s), 2063 (vs), 1993 (vs), 1966 (vs), 1922 (sh), 1878 (sh), 1593 (ms), 1564 (m) cm^{-1}. Stirring was resumed for 20 min followed by the removal of solvent under reduced pressure. The red-brown residue was extracted with 3 × 30 mL of *n*-pentane, and the pale yellow extracts were filtered. Concentration of the filtrate to ca. 10 mL under reduced pressure followed by slow cooling to −70 °C afforded feathery chiffon-yellow crystals. The pale yellow mother liquor was decanted, and the crystalline solid was dried under reduced pressure to give 0.364 g of pastel yellow $[Fe(CO)_4(CNC_6H_5)]$[31] (1.34 mmol, 41.5% relative to Collman's reagent). IR (*n*-pentane): 2163 (m), 2063 (s), 1998 (s), 1972 (vs), 1937 (w) cm^{-1}. MS: parent ion at *m/e* = 271.

Reaction of $Na_2[Fe(CO)_4]\cdot 1.5p$-Dioxane with CH_3NCS and Isolation of $[Fe(CO)_4(CNCH_3)]$. A 6.88 M solution of CH_3NCS

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in THF (0.77 mL, 5.3 mmol) was syringed into a stirred suspension of $Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane (0.917 g, 2.65 mmol) in 20 mL of THF at 4 °C in the absence of light. The reaction mixture gradually darkened over 2.5 h to give a ruddy orange suspension, which was then permitted to settle. IR spectra of the supernatant contained the following absorptions: 2223 (m), 2070 (s), 1987 (s), 1961 (vs), 1925 (m), 1878 (ms), 1774 (mw, br), 1588 (mw), and 1560 (w) cm^{-1}. The mixture was stirred for an additional 30 min and then stripped of solvent under reduced pressure below 0 °C. Extraction with 3 × 30 mL of *n*-pentane at 0 °C followed by concentration of the filtrate to ca. 10 mL under reduced pressure and slow cooling to −70 °C provided clear yellow-white crystalline plates. After the mother liquor had been decanted, the solid was briefly dried in vacuo to yield 0.134 g of $[Fe(CO)_4(CNCH_3)]$[31] (0.64 mmol, 24.2% relative to Collman's reagent). IR (*n*-pentane): 2210 (s), 2071 (s), 1997 (s), 1970 (s), 1935 (m) cm^{-1}. MS: parent ion at m/e = 209.

Reaction of $Li_2[Cr(CO)_5]$ with PhNCS and Isolation of $[Cr(CO)_5(CNC_6H_5)]$. Colorless PhNCS (0.19 mL, 0.21 g, 1.59 mmol) was syringed into a stirred 0.038 M solution of $Li_2[Cr(CO)_5]$ in THF (21.3 mL, 0.81 mmol) at −78 °C. The homogeneous deep red solution was stirred for 5 min and then warmed to room temperature. Solution IR spectra showed ν_{CO} absorptions at 2154 (mw), 2072 (m), 1988 (sh), 1960 (s), 1922 (m), 1886 (s), and 1797 (m) cm^{-1}. After 48 h, IR spectra showed that the bands at 2153, 2070, and 1958 cm^{-1} had intensified at the expense of the ν_{CO} absorptions at lower frequency. Solvent was removed under reduced pressure, and the residue was extracted with 3 × 25 mL of *n*-pentane. The filtered solution was evaporated under reduced pressure to give 0.225 g of a yellow-white solid. Naphthalene was sublimed away from the crude product mixture at room temperature (0.02 Torr, 1.5 h) and then at 35 °C (30 min). Powdery white $[Cr(CO)_5(CNC_6H_5)]$[32] was isolated by sublimation (0.02 Torr, 60–95°C, 1 h) onto a liquid nitrogen-cooled cold finger (0.033 g, 0.11 mmol, 13.9% relative to $[Cr(CO)_5(NMe_3)]$. IR (*n*-pentane): 2138 (w), 2057 (mw), 1963 (s) cm^{-1}. MS: parent ion at m/e = 295.

Reaction of $Li_2[W(CO)_5]$ with MeNCS and Spectroscopic Observation of $[W(CO)_5(CNCH_3)]$. Neat liquid MeNCS (0.22 mL, 0.24 g, 3.22 mmol) was syringed into a vigorously stirred 0.024 M solution of $Li_2[W(CO)_5]$ in THF (22.3 mL, 0.54 mmol) at −78 °C. When warmed to room temperature the homogeneous golden amber mixture darkened to a clear orange. Solution IR spectra showed quantitative consumption of starting material and the appearance of ν_{CO} absorptions at 2200 (m), 2120 (m), 2077 (m), 1984 (sh), 1943 (vs), and 1866 (w) cm^{-1}. Solvent was removed under reduced pressure, and the orange-brown residue was extracted with 3 × 10 mL of *n*-pentane. The faintly yellow extracts were filtered, and solvent was again evaporated under reduced pressure to give 0.349 g of pale yellow powder. Solution IR and mass spectra indicated the presence of $[W(CO)_5(CNCH_3)]$[33] as the only detectable metal carbonyl product in this sample. IR (*n*-pentane): 2183 (w), 2079 (mw), 1956 (vs), 1923 (vw) cm^{-1}. MS: parent ion at m/e = 365.

Preparation of $[W(CO)_5(CNC_6H_5)]$ by Sequential Reaction of $Na_2[W(CO)_5]$ with PhNCS and ClCOCOCl. Clear, colorless PhNCS (57 μL, 0.064 g, 0.47 mmol) was injected into a stirred 0.026 M solution of $Na_2[W(CO)_5]$ in THF (20 mL, 0.52 mmol) at −78 °C. IR spectra of the resultant deep burgundy red solution showed quantitative consumption of the monomeric dianion and the appearance of ν_{CO} absorptions at 2063 (vw), 1986 (mw), 1918 (m), 1875 (s), 1755 (m), and 1510 (m) cm^{-1}. Oxalyl chloride (ClCOCOCl, 42 μL, 0.061 g, 0.48 mmol) was injected into the stirred solution, which darkened to an opaque red-brown color. After 5 min solution IR spectra exhibited absorptions at 2148 (w), 2064 (mw), 2010 (sh), 1970 (sh), 1950 (sh), 1927 (s), and 1886 (sh) cm^{-1}. The mixture was warmed to room temperature, the solvent was removed under reduced pressure, and the red-brown residue was extracted with 3 × 25 mL of *n*-pentane. IR spectra of the filtered extracts indicated the presence of trace $[W(CO)_6]$ (1986 cm^{-1}) together with a major species exhibiting ν_{CO} absorption at 2141 (w), 2061 (m), 1962 (s), and 1930 (w) cm^{-1}. Evaporation of solvent under reduced pressure provided a pale buff-colored powder, from which naphthalene and $[W(CO)_6]$ were sublimed (0.02 Torr, 40 °C, 1 h). Extraction of the pale tan residue with 10 mL of *n*-pentane followed by removal of solvent from the filtrate under reduced pressure afforded powdery cream-colored $[W(CO)_5(CNC_6H_5)]$[32] (0.012 g, 0.03 mmol, 5.9% relative to $[W(CO)_5(NMe_3)]$. IR (*n*-pentane): 2141 (vw), 2060 (mw), 1962 (vs) cm^{-1}. IR (THF): 2148 (w), 2064 (mw), 1953 (ms) cm^{-1}. MS: parent ion at m/e = 427.

Reaction of $Na_2[W(CO)_5]$ with PhNCO and Spectroscopic Quantification of the Product $[W(CO)_6]$ and $[W(CO)_5(CNC_6H_5)]$. Injection of PhNCO (0.23 mL, 0.252 g, 2.11 mmol) into a stirred 0.021 M solution of $Na_2[W(CO)_5]$ in THF (25.1 mL, 0.53 mmol) at −78 °C produced a pale yellow suspension containing fine white filaments. After 5 min, the reaction mixture was warmed to room temperature. IR spectra of the homogeneous yellow solution indicated quantitative consumption of $Na_2[W(CO)_5]$ and formation of $[W(CO)_6]$ (ν_{CO} = 1973 cm^{-1}) together with weaker bands at 2064 (sh), 2055 (vw), 1907 (m), 1712 (m), 1690 (mw, br), and 1580 (m, br) cm^{-1}. When a second portion of PhNCO (0.111 mL, 0.121 g, 1.01 mmol) was added, the IR spectra showed the intensification of absorptions at 2145, 2064, 1973 and 1712 cm^{-1} and diminution of the 1907 cm^{-1} band. The two highest frequency absorptions are superimposable upon those of $[W(CO)_5(CNC_6H_5)]$ in THF, and absorbance mode IR spectra (assuming $\epsilon = 2400\ M^{-1}\ cm^{-1}$ for the 2064 cm^{-1} band) were used to calculate a $[W(CO)_5(CNC_6H_5)]$ concentration of 0.96 mM (4.5% yield relative to $[W(CO)_5(NMe_3)]$). A 1.0-mL aliquot was diluted to 3.0 mL with THF, and absorption spectra (assuming $\epsilon = 14{,}400\ M^{-1}\ cm^{-1}$ for the 1973 cm^{-1} band) were used to calculate a $[W(CO)_6]$ concentration of 5.87 mM. This was extrapolated to 17.6 mM in the original mixture (83.4% yield relative to $[W(CO)_5(NMe_3)]$).

Reaction of $Na_2[Fe(CO)_4]\cdot 1.5p$-Dioxane with PhNCNPh and Isolation of $[Fe(CO)_4(CNC_6H_5)]$. Neat diphenyl carbodiimide (PhNCNPh, 0.58 mL, 0.632 g, 3.25 mmol) was injected into a stirred suspension of $Na_2[Fe(CO)_4]\cdot 1.5p$-dioxane (0.558 g, 1.61 mmol) in 20 mL of THF at ambient temperature. The mixture was refluxed gently for 20 min, and the deep red-brown suspension was permitted to cool and settle. IR spectra of the supernatant showed absorptions at 2164 (mw), 2103 (w), 2060 (s), 2010 (sh), 1986 (sh), 1964 (s), 1918 (s), 1898 (s), 1879 (s), 1660 (ms), and 1592 (s) cm^{-1}. Solvent was removed under reduced pressure, and the red-brown residue was extracted with 2 × 20 mL of toluene. IR spectra of the filtered extracts indicated the presence of $[Fe(CO)_4(CNC_6H_5)]$ (2162 (mw), 2059 (s), 1993 (m), and 1963 (s) cm^{-1} and contained weaker bands at 2105 (w) and 1663 (mw) cm^{-1}. Solvent was evaporated under reduced pressure at 40 °C, and the residue was extracted with 3 × 20 mL of *n*-pentane. Removal of pentane from the filtered extracts under vacuum provided pale yellow prismatic crystals of $[Fe(CO)_4(CNC_6H_5)]$[31] (0.042 g, 0.15 mmol, 9.6% relative to Collman's reagent). IR (*n*-pentane): see above.

Results and Discussion

We were particularly intrigued by the possibility that reductive disproportionation of heteroallenes by dianionic carbonylmetalates could provide direct, convenient syntheses of monothiocarbonyl and monoisonitrile complexes, and our experiments therefore focused on heteroallenes that might be reduced to thiocarbonyl or isonitrile ligands. These include carbon disulfide, carbonyl sulfide, thioisocyanates, isocyanates, and carbodiimides, and Table I summarizes the results of reactions with these substrates which gave rise to characterized organometallic products.

Reactions of Carbon Disulfide with Dianionic Carbonylmetalates. We have previously reported that CS_2 forms a 1:1 adduct with $M_2[W(CO)_5]$ (M = Li or Na),[3] and we have confirmed that excess dry CS_2 shows no tendency to abstract an S^{2-} ion from these adducts in THF over 24 h at room temperature, as indicated by the failure to see IR absorptions corresponding to those of $[W(CO)_5(CS)]$,[34] although there was some deterioration of the

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Table I. Characterized Organometallic Products from the Reductions of Carbonyl Sulfide, Thioisocyanates, Isocyanates, and Carbodiimides with Dianionic Carbonylmetalates

heteroallene	dianionic carbonylmetalate	initial product (solution yield, %)	isolated product (yield, %)
COS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_5]$ (73)	$[Fe(CO)_4I_2]$ (72)
COS	$Na_2[Ru(CO)_4]$	$[Ru(CO)_5]$	$[Ru(CO)_4I_2]$ (72)
COS	$Na_2[Cr(CO)_5]$	$[Cr(CO)_6]$	$[N(n\text{-}Bu)_4][Cr(CO)_5Br]$ (82)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (74)	$[N(n\text{-}Bu)_4][W(CO)_5Br]$ (57)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$ (61)
PhNCS	$Na_2[Fe(CO)_4]$		$[Fe(CO)_4(CNPh)]$ (42)
MeNCS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_4(CNCH_3)]$	$[Fe(CO)_4(CNCH_3)]$ (24)
PhNCS	$Li_2[Cr(CO)_5]$		$[Cr(CO)_5(CNPh)]$ (14)
PhNCO	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (84) + $[W(CO)_5(CNPh)]$ (5)	
PhNCHPh	$Na_2[Fe(CO)_4]$		$[Fe(CO)_4(CNPh)]$ (10)

adduct over this time scale with ν_{CO} absorptions appearing at 1987 and 1811 cm^{-1}. We have also examined the reaction of 4 equiv of dry CS_2 with $Na_2[Fe(CO)_5]\cdot 1.5p$-dioxane in THF at 25 °C, and although this results in an immediate reaction to give an intense deep red-brown solution, there was no infrared evidence after 21 h for formation of $[Fe(CO)_4(CS)]$[35] and no tractable organometallic products could be isolated from the reaction mixture.

Reduction of Carbonyl Sulfide by Dianionic Carbonylmetalates. Since S^{2-} is a weaker base than O^{2-},[36] it would also be expected to be a better leaving group,[37] and the failure to observe reduction of CS_2 by representative dianionic carbonylmetalates of the group 6 and 8 metals therefore suggested that formation of the strong CO triple bond provides an important component of the driving force for the observed reductive disproportionation of CO_2 by these dianions. Consistent with this, sodium salts of tetracarbonyl dianions of the group 8 metals ($[Fe(CO)_4]^{2-}$ and $[Ru(CO)_4]^{2-}$) and pentacarbonyl dianions of the group 6 metals ($[Cr(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$) reacted readily with COS to give the corresponding pentacarbonyls and hexacarbonyls as summarized by the data in Table I.

The reactions were initially monitored by solution IR, and spectroscopic yields of $[Fe(CO)_5]$ and $[W(CO)_6]$ were determined by absorbance mode IR. Determination of isolated product yields was, however, difficult in all four cases: $[Fe(CO)_5]$ is a volatile liquid, $[Ru(CO)_5]$ is unstable with respect to $[Ru_3(CO)_{12}]$,[26] and $[Cr(CO)_6]$ and $[W(CO)_6]$ are volatile and difficult to separate from the naphthalene present as a byproduct of the naphthalenide reduction used to prepare the pentacarbonyl dianions. These problems could, however, be circumvented in each case by chemical derivatization—the group 8 pentacarbonyls were oxidized with I_2 to the more stable and less volatile diiodides *cis*-$[M(CO)_4I_2]$,[25,26] while the hexacarbonyls of the group 6 metals were converted to the corresponding pentacarbonyl bromide anions by oxidative removal of CO with Me_3NO in the presence of $[N(n\text{-}Bu)_4]Br$. It did, however, also prove possible to isolate the pure carbonyl in the case of $[W(CO)_6]$, and the 61% yield obtained was comparable to that indicated by the chemical derivatization method.

We have previously established that reduction of carbon dioxide to coordinated carbon monoxide by dianionic carbonylmetalates of the group 6 and group 8 metals is accompanied by the formation of equivalent quantities of carbonate ion.[3] This would suggest that the reactions of these dianions with COS should be accompanied by equimolar formation of $Na_2[COS_2]$. Dithiocarbonate salts are, however, unstable with respect to disproportionation to carbonate and trithiocarbonate,[38] and this complicated analysis of the inorganic products of the reaction, although mull IR spectra of the precipitates from the crude reaction mixtures did contain broad absorptions at 1440 cm^{-1} matching those of $Na_2[CO_3]$ and a sharper band at 904 cm^{-1} comparable to the principle absorption of an authentic sample of $Na_2[CS_3]\cdot H_2O$. The quantities of these precipitates were consistent with those anticipated, suggesting the stoichiometries in eq 3 and 4.

$$[M(CO)_4]^{2-} + 2COS \rightarrow [M(CO)_5] + COS_2^{2-} \qquad (3)$$

$$M = Fe, Ru$$

$$[M(CO)_5]^{2-} + 2COS \rightarrow [M(CO)_6] + COS_2^{2-} \qquad (4)$$

$$M = Cr, W$$

Attempts to spectroscopically observe an intermediate η^1-COS complex in a reduction reaction were only marginally successful. When 1 equiv of COS was gradually condensed into a −78 °C solution containing $Li_2[W(CO)_5]$, the reaction mixture immediately faded to an orange yellow color. IR spectra indicated the presence of $[W(CO)_6]$ but also contained absorptions at 1884 (vs) and 1859 (m) cm^{-1} indicative of a more electron-rich intermediate complex. The positions and intensities of these absorptions are similar to those which we previously reported for the carbonyl stretching absorptions of $Li_2[W(CO)_5(CO_2)]$,[3] consistent with formulation of this species as $Li_2[W(CO)_5(COS)]$, but the thermally unstable species could not be prepared without considerable contamination by $[W(CO)_6]$, suggesting that it is so reactive that it reacts with incoming COS as fast as it is formed. The observation of an intermediate in reactions using 1 equiv of COS does, however, support the stoichiometry in eq 4, and argues against direct sulfide extrusion from a COS complex.

The reactions of COS with dianionic carbonylmetalates are very sensitive to the presence of water in the COS, and we found it essential to dry commercial COS (see Experimental Section). Undried COS resulted in protonation of the dianions to form hydrido monoanions $[M(CO)_4H]^-$ (M = Fe[39] or Ru[40]) or $[M(CO)_5H]^-$ (M = Cr[41] or W[42]). In the case of the group 8 metals IR spectroscopy indicated that the hydrides were unreactive toward COS, while in the case of the group 6 metals they resulted in competitive formation of the monothioformate complexes $Na[M(CO)_5SC(O)H]$, presumably by insertion into the metal–hydride bonds.[27,29]

Reduction of Isothiocyanates with Dianionic Carbonylmetalates. Results to this point suggested that

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sulfide could be extracted from dianionic η^1-heteroallene complexes by excess heteroallene as long as the reaction generated a strong CX triple bond. Since the C≡N bond (ca. 212 kcal mol^{-1}[43]) is intermediate in strength between the C≡O band (256 kcal mol^{-1}[43]) and the C≡S bond (166 kcal mol^{-1}[44]), it seemed possible that reductive disproportionation of isothiocyanates could provide a clean route to monoisonitrile complexes, and we therefore investigated the reaction of tetracarbonyl dianions of the group 8 metals and pentacarbonyl dianions of the group 6 metals with phenyl isothiocyanate and methyl isothiocyanate.

The most promising isothiocyanate reductions were those with Collman's reagent. A suspension of $Na_2[Fe(CO)_4]\cdot 1.5$*p*-dioxane in THF reacted with 2 equiv of PhNCS over about 1 h to give a dark precipitate under a deep red solution, from which the known isonitrile complex $[Fe(CO)_4(CNC_6H_5)]$[31] could be isolated in 42% yield. The previous thermal route to this complex gives the product in only moderate yields, and reductive disproportionation of PhNCS provides a competitive route to this material. An analogous reaction of Collman's reagent with CH_3NCS again led to the monoisonitrile complex ($[Fe(CO)_4(CNCH_3)]$,[31] but the yield from the alkyl isothiocyanate was not as good as it had been from the aryl isothiocyanate, and the product could only be isolated in 24% yield.

In both cases IR spectra indicated quantitative consumption of the 2 equiv of isothiocyanate used in the reaction, consistent with description of the reactions as reductive disproportionations of the heteroallenes by the dianionic carbonylmetalate (eq 5). The final fate of the

$$Na_2[Fe(CO)_4] + 2RNCS \rightarrow [Fe(CO)_4(CNR)] + Na_2[RNCS_2] \quad (5)$$

dithiocarbimate which we would expect to be the coproduct was not, however, determined, and the reaction is not general for all R groups—only traces (IR) of $[Fe(CO)_4(CN\text{-}t\text{-}Bu)]$[31] were formed when excess *t*-BuNCS was refluxed with $Na_2[Fe(CO)_4]\cdot 1.5$*p*-dioxane in THF for 18 h.

Attempts to extend the Collman's reagent reactions to the reduction of PhNCS with $Na_2[Ru(CO)_4]$ did not lead to a Ru isonitrile complex, and solution IR spectra of the deep red suspension obtained after 11 h at ambient temperatures indicated the presence of unreacted PhNCS and the formation of an unidentified carbonyl containing compound with absorptions at 2060 (vw), 2005 (s), 1982 (s), and 1933 (s, br) cm^{-1}. No tractable organometallic product could be isolated from the solution.

The reactions of isothiocyanates with the pentacarbonylmetalates of the group 6 metals were less experimentally straightforward than the reactions with $[Fe(CO)_4]^{2-}$. Solutions of $Li_2[Cr(CO)_5]$ did react with 2 equiv of PhNCS over 2 days to give the monoisonitrile complex $[Cr(CO)_5(CNC_6H_5)]$,[31] but isolated yields were only modest (14%). IR spectra of the crude product suggested that the initial yield was significantly higher, but the fractional sublimation required to separate the complex from naphthalene resulted in significant purification losses.

$$Li_2[Cr(CO)_5] + 2PhNCS \rightarrow [Cr(CO)_5(CNPh)] + Li_2[PhNCS_2] \quad (6)$$

Addition of CH_3NCS (6 equiv) to a solution of $Li_2[W(CO)_5]$ also resulted in consumption of the starting dianion (IR), and ν_{CO} absorptions appeared consistent with the formation of a monoisonitrile, $[W(CO)_5(CNCH_3)]$,[32] as the only carbonyl-containing product. No absorptions attributable to $[W(CO)_5(CS)]$[33] were observed, but the similar solubilities and volatilities of naphthalene and the monoisonitrile complex rendered isolation of the latter impractical.

The reaction of $Li_2[W(CO)_5]$ with excess PhNCS was surprisingly complex. Addition of the heteroallene to a solution of the salt at −78 °C produced a homogeneous deep red solution whose color intensified as the reaction warmed to 25 °C. There was, however, no precipitation of an insoluble inorganic product, and solution IR spectra (although they confirmed consumption of the pentacarbonyl dianion) give no indication that $[W(CO)_5(CNC_6H_5)]$[32] had been formed and no tractable inorganic product could be isolated from this solution. It seemed probable that $[W(CO)_5]^{2-}$ had formed a η^1 complex with the added PhNCS, and we therefore attempted a reaction analogous to that reported by Fehlhammer et al. for the Cr system[19] and added oxalyl chloride to the solution formed by addition of 0.9 equiv of PhNCS to a solution of $Na_2[W(CO)_5]$ in THF at −78 °C. IR spectra of the initial adduct were strikingly similar to those for the reaction of $Li_2[W(CO)_5]$ with excess PhNCS, and subsequent spectra indicated that this adduct reacted with oxalyl chloride (ClCOCOCl) to yield a mixture of the anticipated isonitrile complex $[W(CO)_5(CNC_6H_5)]$[32] (eq 7) and an unidentified species with ν_{CO} absorptions at 1927 (vs) and 1886 (sh) cm^{-1}. The true yield of the isonitrile complex was probably ca. 20%, but spectroscopically pure product could only be isolated in 6% yield because of losses during sublimation.

$$Na_2[W(CO)_5] + PhNCS \rightarrow Na_2[W(CO)_5C(NPh)S] \xrightarrow{C_2Cl_2O_2} [W(CO)_5(CNPh)] + COS + CO + 2NaCl \quad (7)$$

Reactions of Isocyanates with Dianionic Carbonylmetalates. The observation that isonitriles were the only observable products from the reactions of thioisocyanates with dianionic carbonylmetalates, and that there was no tendency to form thiocarbonyl complexes, is consistent with the expectation that the direction of reduction of asymmetric heteroallenes is predominantly controlled by the strength of the triple bond in the C≡X ligand being formed. As pointed out above, however, the C≡N bond, although weaker than a C≡O bond, is much stronger than a C≡S bond, and this raised the possibility that there might not be a strong preference in the direction of reduction of asymmetric heteroallenes in which there were oxo and imido groups at the ends of the heteroallenes. We therefore examined the reactions of aryl and alkyl isocyanates with representative dianionic carbonylmetalates of the group 6 and 8 metals.

As expected, $[W(CO)_6]$ was the principal product of the reaction of phenyl isocyanate (4 equiv) with $Na_2[W(CO)_5]$ in THF with −78 °C. This gave a pale yellow suspension, followed by a homogeneous yellow solution after the mixture had warmed to ambient temperatures. IR spectroscopy established that $[W(CO)_6]$ was the dominant tungsten complex in this solution, together with smaller quantities of $[W(CO)_5(CNC_6H_5)]$,[32] and after the addition of a second portion of PhNCO (2 equiv) to ensure complete reaction, absorbance mode IR indicated solution yields of 84% $[W(CO)_6]$ and 5% $[W(CO)_5(CNPh)]$.

The most reasonable stoichiometry for the reaction by which the $[W(CO)_6]$ had been formed is that in eq 8, but

$$Na_2[W(CO)_5] + 2PhNCO \rightarrow [W(CO)_6] + Na_2[(PhN)_2CO] \quad (8)$$

direct evidence for the consumption of 2 equiv of the isocyanate is lacking. PhNCO tends to trimerize to *N*,-

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[44] Hildebrand, D. L. *Chem. Phys. Lett.* **1972**, *15*, 379.

N′,*N*″-triphenylisocyanurate,[45] and IR spectra of the crude reaction mixture, which indicated complete consumption of the initial 4 equiv of PhNCO, also exhibited a moderately strong absorption at 1712 cm^{-1} which suggested formation of significant quantities of the cyclic trimer.

Competitive cyclotrimerization was an even more significant problem with the group 8 metals, and there was no observable reduction of CH_3NO or PhNCO by Collman's reagent. Addition of either heteroallene (6 equiv) to a THF suspension of Collman's reagent at 25 °C led exclusively to cyclotrimerization,[45,46] suggesting that cyclotrimerization, which is base catalyzed, is faster under these conditions than addition to $[Fe(CO)_4]^{2-}$.

Reactions of Carbodiimides with Collman's Reagent. The reduction of carbodiimides potentially provides an alternative approach to monoisonitrile complexes, but experiments with Collman's reagent suggested that this was not, in practice, a useful reaction. Although the reaction of $Na_2[Fe(CO)_4]\cdot 1.5$*p*-dioxane with PhNCNPh did lead to the formation of $[Fe(CO)_4(CNPh)]$, the isolated yield was small (10%), and, since similar experiments with the cyclohexyl analogue $C_6H_{11}NCNC_6H_{11}$ did not lead to detectable levels of $[Fe(CO)_4(CNC_6H_{11})]$ after 6.5 h at 25 °C, no further experiments were conducted with carbodiimides.

Conclusions

The results above establish that dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes X=C=Y other than CO_2 to coordinated C≡X ligands, provided X is a first-row element (N or O) which can form a strong triple bond with C. We have, for example, seen no cases of formation of a coordinated thiocarbonyl, and the marked preference for the formation of carbonyl ligands rather than isonitriles (as shown by the reaction of $Na_2[W(CO)_5]$ with PhNCO and by the higher yields of carbonyl complexes from reactions with COS than of isonitriles from reduction of thioisocyanates) is consistent with control of the direction of reduction of asymmetric heteroallenes by the relative strengths of the C≡X bands formed. The failure to observe reductive disproportionation of CS_2 suggests that the strength of the C=X bond being cleaved is not an important factor, since the C=S bond is weaker than the C=N and C=O bonds, but in the absence of detailed thermochemical data we cannot rule out the possibility that the strength of the M—C bonds being formed is also important.

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Registry No. COS, 463-58-1; PhNCS, 103-72-0; MeNCS, 556-61-6; PhNCO, 103-71-9; PhNCHPh, 622-16-2; $Na_2[Fe(CO)_4]$, 14878-31-0; $Na_2[Ru(CO)_4]$, 57398-60-4; $Na_2[Cr(CO)_5]$, 52154-81-1; $Na_2[W(CO)_5]$, 54099-82-0; $Li_2[Cr(CO)_5]$, 109283-12-7; $[Fe(CO)_5]$, 13463-40-6; *cis*-$[Fe(CO)_4I_2]$, 14911-55-8; $[Ru(CO)_5]$, 16406-48-7; *cis*-$[Ru(CO)_4I_2]$, 18475-75-7; $[Cr(CO)_6]$, 13007-92-6; [N(*n*-Bu)$_4$][Cr(CO)$_5$Br], 78022-78-3; $[W(CO)_6]$, 14040-11-0; [N(*n*-Bu)$_4$][W(CO)$_5$Br], 67846-99-5; $[Fe(CO)_4(CNPh)]$, 17595-21-0; $[Fe(CO)_4(CNCH_3)]$, 14741-64-1; $[Cr(CO)_5(CNPh)]$, 14782-94-6; $[W(CO)_5(CNPh)]$, 15612-93-8; $Na[Cr(CO)_5SC(O)H]$, 120311-05-9; $Na[W(CO)_5SC(O)H]$, 120311-06-0; ClCOCOCl, 79-37-8.

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AM1 Calculations for Compounds Containing Germanium

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AM1 has been parametrized for germanium. Calculations are reported for a number of compounds of germanium. The results are generally superior to those from MNDO, especially in geometries.

Introduction

Now that germanium is readily available as a result of its importance in electronics, increasing attention is being paid to its chemistry.[1] As a result, there is a growing need for a practical theoretical procedure for studying the behavior of germanium compounds. While ab initio methods are of limited value for studies of elements from the third and later rows of the periodic table, MNDO[2] and AM1[3] have proved effective in this connection. AM1, the most recent of our semiempirical procedures, has been parametrized successfully for the halogens,[4] silicon,[5] zinc,[6] mercury,[7] and phosphorus,[8] as well as boron[9] and the "organic" elements,[3] while MNDO has also been parametrized for all the main group IV elements, including germanium.[10] The errors in the MNDO heats of formation for germanium compounds were, however, larger than usual. Since AM1 has proved generally superior to MNDO, there is clearly a need for it to be extended to germanium. Here we report AM1 parameters for it.

Table I. Optimized AM1 Parameters for Germanium

optimized parameters	AM1	MNDO
U_{ss}, eV	−34.183 889	−33.949 367
U_{pp}, eV	−28.640 811	−27.425 105
ζ_s, au	1.219 631	1.293 180
ζ_p, au	1.982 794	2.020 564
β_s, eV	−4.356 607	−4.516 479
β_p, eV	−0.991 091	−1.755 517
α, Å^{-1}	2.136 405	1.978 498
G_{ss}	10.168 605	9.800 000
G_{pp}	6.671 902	7.300 000
G_{sp}	8.144 473	8.300 000
G_{p2}	6.269 706	6.500 000
H_{sp}	0.937 093	1.300 000

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