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Reactions of $M_2(CO)_9L$ ($M = Re, Mn$; $L = CO, MeCN$) with thioacetamide and thiobenzamide: Facile metal-mediated nitrogen–hydrogen bond activation and subsequent carbon–nitrogen or sulfur–sulfur bond formation

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ABSTRACT

Addition of thioacetamide or thiobenzamide to $Re_2(CO)_{10}$ at room temperature in presence of Me_3NO gives low yields of the simple substitution products $Re_2(CO)_9\{\kappa^1\text{-}S{=}C(R)NH_2\}$ (**1**, R = Me; **2**, R = Ph) in which the acyclic amides are bound through sulfur and occupy an equatorial site. In contrast, Me_3NO initiated reactions of $Mn_2(CO)_{10}$ with the same amides lead to the isolation of hexacarbonyl complexes, $Mn_2(CO)_6\{\mu\text{-}S_2C(R)NH\}_2$ (**3**, R = Me; **4**, R = Ph), crystallographic studies revealing a binuclear core in which $Mn(CO)_3$ moieties are spanned by two RC(SS)NH ligands. When $Mn_2(CO)_9(NCMe)$ is used as the starting material only the mononuclear species $Mn(CO)_4\{\kappa^1{:}\eta^1\text{-}RC(S)NHCO\}$ (**5**, R = Me; **6**, R = Ph) could be isolated. These contain a chelating RC(S)NHCO ligand formed as a result of coupling the deprotonated amides with CO. Crystallographic studies have been carried out on both complexes, a careful inspection of bond lengths and angles within the chelate ring suggesting that a zwitterionic acyl-thiolate resonance structure is most prevalent.

1. Introduction

Reactions of $M_2(CO)_{10}$ (M = Re, Mn) with nitrogen and/or sulfur donor ligands such as thiols [1–3], dithiols [4], heterocyclic thiones or thiolactams [5–12], *N*-containing heterocycles [13–15], derivatives of thiourea [16,17], thioethers [18,19], thioketones [20] and elemental sulfur [21–23] have been thoroughly investigated. The first step in these reactions is generally the displacement of a carbonyl and coordination of the new ligand into an equatorial site. Once within the manifold of the binuclear center secondary rearrangements can then occur. A good example of this comes from the work of Adams and co-workers [17] who showed that reaction of $Re_2(CO)_9(NCMe)$ with $Et_2NC(S)NHAr$ (Ar = *p*-tolyl) proceeds in high yields at 68 °C to give $Re_2(CO)_9\{\kappa^1\text{-}SC(NEt_2)NHAr\}$, which in turn transforms cleanly into $[Re(CO)_3\{\mu\text{-}SC(N\text{-}p\text{-tolyl})(NEt_2)\}]_2$ at 97 °C as a result of N–H bond activation and carbonyl loss (Scheme 1).

To date no reports have documented the reactivity of $M_2(CO)_{10}$ (M = Mn, Re) with acyclic thioamides ($RCSNH_2$), simple molecules that possess both hard and soft donor sites. A literature survey on the reactivity of metal carbonyls toward acyclic thioamides revealed only one example of such reactivity [24]. Thus the phosphinidine clusters, $Fe_3(CO)_{10}(\mu_3\text{-}PR)$ ($R = {}^tBu, {}^iPr$), react with thioacetamide to give the sulfido-capped carbene clusters, $Fe_3(CO)_8\{\eta^1\text{-}C(NH_2)Me\}(\mu_3\text{-}S)(\mu_3\text{-}PR)$ ($R = {}^tBu, {}^iPr$) as a result of carbon–sulfur bond scission at cluster surface [24] (Scheme 2). The facile nature of this carbon–sulfur bond scission supports the idea that this ligand system can in principle be used toward the synthesis of high nuclearity sulfido-capped clusters. With this in mind we have investigated the reactions of dirhenium and dimanganese carbonyls with thioacetamide and thiobenzamide. We find that not only do these dinuclear carbonyls behave differently toward thioamides, but also the isolated products varied when we use different carbonyl complexes of the same metal as starting material.

2. Experimental section

2.1. General data

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Thioacetamide ($MeCSNH_2$) and thiobenzamide ($PhCSNH_2$) were purchased from

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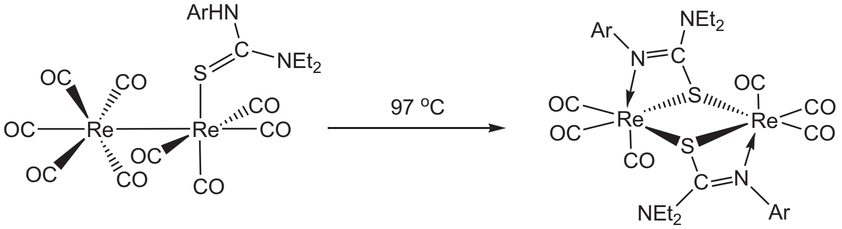


Scheme 1. N–H addition at a dirhenium center.

Aldrich and used as received. $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were purchased from Strem Chemicals Inc. and used without further purification. $Re_2(CO)_9(NCMe)$ and $Mn_2(CO)_9(NCMe)$ were prepared according to the literature methods [25]. Infrared spectra were recorded on a Shimadzu FTIR 8101 or Shimadzu IR Prestige 21 spectrophotometer. NMR spectra were recorded on a Varian 500 instrument. Elemental analyses were performed by BCSIR Laboratories, Dhaka.

2.2. Reaction of $Re_2(CO)_{10}$ with thioacetamide

A CH_2Cl_2 solution (25 mL) of $Re_2(CO)_{10}$ (100 mg, 0.153 mmol), $MeCSNH_2$ (12 mg, 0.160 mmol) and Me_3NO (12 mg, 0.160 mmol) was stirred at room temperature for 7 h. The solvent was removed by rotary evaporation under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed five bands. The first and last bands were unreacted $Re_2(CO)_{10}$ (trace) and $MeCSNH_2$ (trace). The fourth band afforded $Re_2(CO)_9\{\kappa^1\text{-S=C(Me)NH}_2\}$ (**1**) (15 mg, 14%) as colorless crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The content of the other two bands were too small for characterization. Spectral data for **1**: Anal. Calcd for $C_{11}H_5NO_9Re_2S$: C, 18.50; H, 0.71; N, 1.98. Found: C, 18.94; H, 0.76; N, 2.06%. IR (ν(CO), CH_2Cl_2): 2102 m, 2038 s, 1993 vs, 1958 s, 1911 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.83 (br, s, 1H), 7.53 (br, s, 1H), 2.70 (s, 3H).

2.3. Reaction of $Re_2(CO)_9(NCMe)$ with thioacetamide

$MeCSNH_2$ (12 mg, 0.160 mmol) was added to a benzene solution (25 mL) of $Re_2(CO)_9(NCMe)$ (100 mg, 0.150 mmol) and the mixture was then refluxed for 32 h. A similar chromatographic separation described as above gave **1** (12 mg, 11%) after recrystallization from hexane/CH_2Cl_2 at 4 °C.

2.4. Reaction of $Re_2(CO)_{10}$ with thiobenzamide

To a CH_2Cl_2 solution (25 mL) of $Re_2(CO)_{10}$ (100 mg, 0.153 mmol) was added $PhCSNH_2$ (22 mg, 0.160 mmol) and Me_3NO (12 mg, 0.160 mmol) and the mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed one major and several minor bands. The major band afforded $Re_2(CO)_9\{\kappa^1\text{-S=C(Ph)NH}_2\}$ (**2**) (16 mg, 14%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The content of the other minor bands were too small for characterization. Spectral data for **2**: Anal. Calcd for $C_{16}H_7NO_9Re_2S$: C, 24.98; H, 0.92; N, 1.82. Found: C, 25.36; H, 0.97; N, 1.87%. IR (ν(CO), CH_2Cl_2): 2107 w, 2037 s, 1994 s, 1934 m, 1915 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.95 (br, s, 1H), 7.89 (br, s, 1H), 7.77 (m, 2H), 7.59 (m, 1H), 7.46 (m, 2H).

2.5. Reaction of $Re_2(CO)_9(NCMe)$ with thiobenzamide

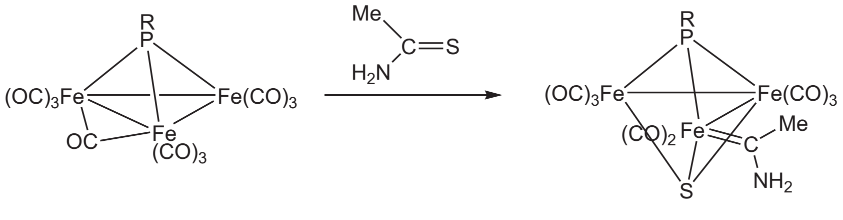
$PhCSNH_2$ (22 mg, 0.160 mmol) was added to a benzene solution (25 mL) of $Re_2(CO)_9(NCMe)$ (100 mg, 0.150 mmol) and the mixture was then refluxed for 24 h. A similar chromatographic separation described as above gave **2** (11 mg, 10%) after recrystallization from hexane/CH_2Cl_2 at 4 °C.

2.6. Reaction of $Mn_2(CO)_{10}$ with thioacetamide

To a CH_2Cl_2 solution (25 mL) of $Mn_2(CO)_{10}$ (100 mg, 0.256 mmol) was added $MeCSNH_2$ (20 mg, 0.266 mmol) and Me_3NO (40 mg, 0.532 mmol) and the mixture was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed three bands. The faster moving band afforded $Mn_2(CO)_6\{\mu\text{-S}_2\text{C(Me)NH}\}_2$ (**3**) (11 mg, 9%) as orange crystals, while the slower moving band gave $Mn(CO)_4\{\kappa^1{:}\eta^1\text{-MeC(S)NHCO}\}$ (**5**) (3 mg, 2%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The content of the other band was too small for characterization. Spectral data for **3**: Anal. Calcd for $C_{10}H_8Mn_2N_2O_6S_4$: C, 24.49; H, 1.65; N, 5.71. Found: C, 25.14; H, 1.73; N, 5.76%. IR (ν(CO), CH_2Cl_2): 2039 m, 2019 vs, 1993 vw, 1932 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.06 (br. s, 2H), 2.36 (s, 6H). Spectral data for **5**: Anal. Calcd for $C_7H_4MnNO_5S$: C, 31.24; H, 1.50; N, 5.21. Found: C, 31.67; H, 1.56; N, 5.28%. IR (ν(CO), CH_2Cl_2): 2085 m, 1997 vs, 1970 s, 1921 vw, 1657 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.94 (br, s, 1H), 2.72 (s, 3H).

2.7. Reaction of $Mn_2(CO)_9(NCMe)$ with thioacetamide

$MeCSNH_2$ (20 mg, 0.266 mmol) was added to a CH_2Cl_2 solution (25 mL) of $Mn_2(CO)_9(NCMe)$ (100 mg, 0.248 mmol) and the mixture was then stirred at room temperature for 4 h. A similar chromatographic separation described as above gave **5** (13 mg, 10%) after recrystallization from hexane/CH_2Cl_2 at 4 °C.



Scheme 2. C–S addition at a triiron center.