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Building of dithiocarbamate and dithiocarbimate ligands within a heterobimetallic core

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Heterobinuclear anions $[MnRe(CO)_6(\mu\text{-}S)(\mu\text{-}SCPR_3)]^{2-}$ (**2**) undergo selective protonation and electrophilic addition of dimethylthiocarbamoyl or isothiocyanate to afford, respectively, neutral $[MnRe(CO)_6(\mu\text{-}S_2CNMe_2)(\mu\text{-}S_2CPR_3)]$ (**3**) containing μ_2-(S,S′) dithiocarbamate, or anionic $[MnRe(CO)_6(\mu\text{-}SC(S)NR')\{\mu\text{-}SC(H)PR_3\}]^-$ (**4**) containing μ_2-(*N*,*S*)-dithiocarbimate. The terminal sulfur in the latter can be methylated with MeI or metallated with $[AuCl(p\text{-tolyl})_3]$ to give neutral dithiocarbimato complexes **5** or **6**. The structures of **3a** (R = Pr^i), **5a** (R = Pr^i, R′= Et), and **5c** (R = Pr^i, R′= Ph), have been determined by X-ray crystallography.

Introduction

Extensive studies have been carried out on the stoichiometric processes of transition metal-promoted C–S bond formation and cleavage, mainly aiming to model individual steps of different metal-catalyzed organic synthesis.[1] Seyferth studied the reactivity of thiolate-bridged diiron carbonyl anionic complexes toward sulfur-containing organic electrophiles, such as *N*,*N*-dimethyldithiocarbamoyl chloride, carbon disulfide or isothiocyanates.[2] The related reactivity of heterobimetallic complexes remains virtually unexplored. We have shown that the reduction of complexes $[MnRe(CO)_6(\mu\text{-}S_2CPR_3)]$ (**1a**–**b**) with sodium amalgam occurs with cleavage of the Mn–Re and one C–S bond, to afford anionic complexes (**2a**–**b**) with the two resulting metal fragments bridged by the S and $SCPR_3$ ligands (See Chart 1).[3–4]

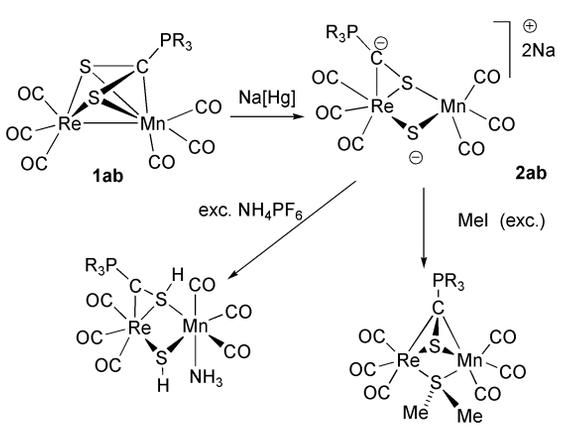

Chart 1

These anions undergo electrophilic addition, and the site of the attack appears to be strongly dependent on the incoming group. Thus, treatment with excess NH_4PF_6 leads to the protonation at the sulfur and carbon atoms, producing SH^- and $R_3PC(H)S^-$ ligands. In contrast, reaction with excess MeI produces double methylation at the sulfur atom, giving a dimethyl sulfide bridge.[5] In view of the paucity of systematic studies on heterobinuclear complexes we considered of interest to explore the reactivity of carbonyl anions **2a**–**b** towards organic electrophiles. We report here the observation of size-controlled regioselective addition of electrophiles to afford new complexes with organic ligands produced through C–S coupling within the coordination sphere of the heterometallic system.

Results and discussion

A solution of the anionic complexes $Na_2[MnRe(CO)_6(\mu\text{-}S)(\mu\text{-}SCPR_3)]$ (**2a**–**b**), freshly prepared from $[MnRe(CO)_6(\mu\text{-}S_2CPR_3)]$ (**1a**–**b**) and sodium amalgam, reacted instantaneously with one molar equivalent of dithiocarbamoyl chloride at −78 °C to afford the neutral complexes $[MnRe(CO)_6(\mu\text{-}S_2CNMe_2)(\mu\text{-}S_2CPR_3)]$ (**3a**–**b**) which were isolated as orange crystalline solids.

An X-ray determination (see Fig. 1, and Tables 1 and 2) showed that the molecule of **3a** consists of the fragments $Mn(CO)_3$ and $Re(CO)_3$ bridged by the ligands triisopropylphosphoniothiolateylide, $SC(H)PPr^i_3$, and dithiocarbamate, S_2CNMe_2. The analytical and spectroscopic data in solution (see the Experimental) are consistent with the solid state structure.

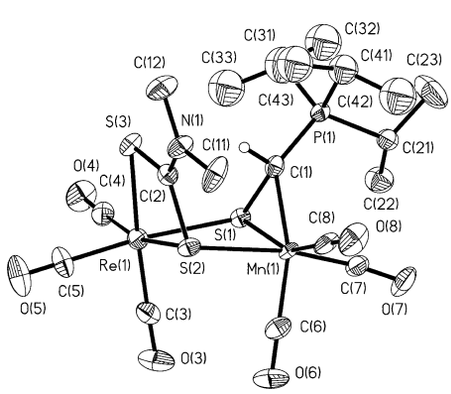

Fig. 1 Perspective view of the molecule of $[MnRe(CO)_6(\mu\text{-}S_2CNMe_2)\{\mu\text{-}SC(H)PPr^i_3\}]$ (**3a**), showing the atom numbering.

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Table 1 Crystal data and refinement details for $[MnRe(CO)_6(\mu\text{-}S_2CNMe_2)\{\mu\text{-}SC(H)PPr^i_3\}]$ (**3a**), $[MnRe(CO)_6\{\mu\text{-}SCS(Me)NEt\}\{\mu\text{-}SC(H)PPr^i_3\}]$ (**5a**), and $[MnRe(CO)_6\{\mu\text{-}SCS(Me)NPh\}\{\mu\text{-}SC(H)PPr^i_3\}]$ (**5c**)

	Compound **3a**	Compound **5a**	Compound **5c**
Formula	$C_{19}H_{28}MnNO_6PReS_3$	$C_{20}H_{30}MnNO_6PReS_3$	$C_{24}H_{30}MnNO_6PReS_3$
Fw	734.71	748.74	796.78
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1n$ (No. 14)
a/Å	9.334(1)	11.146(4)	10.902(5)
b/Å	10.872(1)	16.565(5)	17.048(8)
c/Å	15.337(4)	15.537(5)	16.551(8)
α/°	72.04(1)	90	90
β/°	86.19(1)	103.36(1)	98.263(8)
γ/°	65.95(2)	90	90
V/Å^3	1348.9(5)	2790(2)	3044(2)
Z	2	4	4
T/K	296	299	299
ρ_{calc}/g cm^{-3}	1.809	1.782	1.739
μ/mm^{-1}	5.275	5.101	4.682
Refl. measured	5145	11992	13339
Refl. independent	4722	4028	4388
Refl. observed, $I \leq 2\sigma(I)$	2668	3422	3611
R, wR_2	0.0603, 0.1604	0.0220, 0.0525	0.0313, 0.0790

Table 2 Selected interatomic distances (Å), and angles (°) in $[MnRe(CO)_6(\mu\text{-}S_2CNMe_2)\{\mu\text{-}SC(H)PPr^i_3\}]$ (**3a**)

Re(1)–C(3)	1.852(19)	Re(1)–C(4)	1.918(19)
Re(1)–C(5)	1.926(18)	Re(1)–S(3)	2.488(4)
Re(1)–S(2)	2.507(4)	Re(1)–S(1)	2.514(4)
Mn(1)–C(7)	1.763(18)	Mn(1)–C(6)	1.782(18)
Mn(1)–C(8)	1.808(18)	Mn(1)–C(1)	2.103(15)
Mn(1)–S(1)	2.310(4)	Mn(1)–S(2)	2.518(5)
S(1)–C(1)	1.792(14)	S(2)–C(2)	1.757(16)
S(3)–C(2)	1.684(15)	P(1)–C(1)	1.746(15)
N(1)–C(2)	1.311(19)	N(1)–C(12)	1.43(2)
N(1)–C(11)	1.51(2)	C(3)–O(3)	1.19(2)
C(4)–O(4)	1.15(2)	C(5)–O(5)	1.11(2)
C(6)–O(6)	1.165(19)	C(7)–O(7)	1.19(2)
C(8)–O(8)	1.181(19)		
C(3)–Re(1)–S(3)	172.1(6)	C(4)–Re(1)–S(3)	98.0(5)
C(5)–Re(1)–S(3)	90.2(6)	C(3)–Re(1)–S(2)	101.9(6)
C(4)–Re(1)–S(2)	166.8(5)	C(5)–Re(1)–S(2)	94.5(5)
S(3)–Re(1)–S(2)	70.16(13)	C(3)–Re(1)–S(1)	86.4(6)
C(5)–Re(1)–S(1)	173.4(6)	S(3)–Re(1)–S(1)	92.52(13)
S(2)–Re(1)–S(1)	80.78(13)	C(6)–Mn(1)–C(1)	154.9(7)
C(8)–Mn(1)–S(1)	155.6(5)	C(1)–Mn(1)–S(1)	47.6(4)
C(7)–Mn(1)–S(2)	170.7(5)	C(1)–S(1)–Mn(1)	60.1(5)
C(1)–S(1)–Re(1)	110.5(5)	Mn(1)–S(1)–Re(1)	98.01(14)
C(2)–S(2)–Re(1)	87.2(5)	C(2)–S(2)–Mn(1)	111.0(5)
Re(1)–S(2)–Mn(1)	92.96(13)	C(2)–S(3)–Re(1)	89.5(6)

Table 3 Selected interatomic distances (Å), and angles (°) in $[MnRe(CO)_6\{\mu\text{-}SCS(Me)NEt\}\{\mu\text{-}SC(H)PPr^i_3\}]$ (**5a**)

Re(1)–C(5)	1.865(5)	Re(1)–C(4)	1.883(5)
Re(1)–C(3)	1.890(5)	Re(1)–C(1)	2.187(3)
Re(1)–S(1)	2.4252(12)	Re(1)–S(2)	2.5755(12)
Mn(2)–C(6)	1.792(5)	Mn(2)–C(7)	1.811(5)
Mn(2)–C(8)	1.818(5)	Mn(2)–N(1)	2.096(4)
Mn(2)–S(1)	2.4507(12)	Mn(2)–S(2)	2.4532(12)
S(1)–C(1)	1.807(3)	S(2)–C(2)	1.763(4)
S(3)–C(2)	1.750(4)	S(3)–C(10)	1.770(7)
P(1)–C(1)	1.779(3)	N(1)–C(2)	1.274(5)
C(4)–Re(1)–C(3)	93.01(19)	C(5)–Re(1)–C(1)	101.44(15)
C(4)–Re(1)–C(1)	110.36(18)	C(3)–Re(1)–C(1)	155.13(15)
C(4)–Re(1)–S(1)	155.89(15)	C(3)–Re(1)–S(1)	110.14(12)
C(1)–Re(1)–S(1)	45.77(9)	C(5)–Re(1)–S(2)	170.33(13)
C(1)–Re(1)–S(2)	86.21(9)	S(1)–Re(1)–S(2)	82.05(4)
C(6)–Mn(2)–N(1)	167.16(17)	C(7)–Mn(2)–N(1)	103.63(18)
C(8)–Mn(2)–N(1)	90.60(16)	C(8)–Mn(2)–S(1)	179.56(15)
C(7)–Mn(2)–S(2)	168.47(14)	N(1)–Mn(2)–S(2)	67.31(11)
S(1)–Mn(2)–S(2)	84.09(4)	C(1)–S(1)–Re(1)	60.15(11)
C(1)–S(1)–Mn(2)	110.80(12)	Re(1)–S(1)–Mn(2)	95.89(4)
C(2)–S(2)–Mn(2)	77.27(16)	C(2)–S(2)–Re(1)	109.93(12)
Mn(2)–S(2)–Re(1)	92.07(4)	C(2)–S(3)–C(10)	103.0(3)
C(2)–N(1)–C(11)	123.1(4)	C(2)–N(1)–Mn(2)	103.0(3)
C(11)–N(1)–Mn(2)	133.9(4)	P(1)–C(1)–S(1)	117.40(19)
P(1)–C(1)–Re(1)	131.72(19)	S(1)–C(1)–Re(1)	74.08(12)

It is apparent from Fig. 1 that **3a** is produced by addition of one mol-equivalent of the thiocarbamoyl group to the sulfur atom splitted from S_2CPR_3, and concurrent protonation of the carbon atom of R_3PCS. Despite repeated attempts to carry out the reaction in anhydrous conditions, it was not possible to avoid the protonation of the carbon atom.

Some other carbon-based neutral electrophiles were used, attempting to gather information of the scope of this reactivity. Thus the reaction of anionic **2a**–**b** with ethyl- or phenyl-isothiocyanate proceeds smoothly to give, according to IR monitoring (see the Experimental), new anions $[MnRe(CO)_6(\mu\text{-}SC(S)NR')\{\mu\text{-}SC(H)PR_3\}]^-$ (**4a**–**d**, in Scheme 1). Their high reactivity precluded its isolation, and they were used *in situ* for further reactions. Freshly prepared solutions of **4a**–**b** react with methyl iodide to afford neutral derivatives $[MnRe(CO)_6\{\mu\text{-}SC(SMe)NR'\}\{\mu\text{-}SC(H)PR_3\}]$ (**5a**–**d**, in Scheme 1), which could be isolated and fully characterized by analytical and spectroscopic methods. The $^{31}P\{^1H\}$ NMR spectra of complexes **5a**–**d** reveal the presence of two isomers, in *ca.* a 10 : 1 ratio. This is consistent with the results of the structural determination as it will be discussed below. Additionally, crystals of **5a** and **5c** were subjected to X-ray analysis, and the results are summarized in Tables 1, 3, and 4, and in Fig. 2 and 3.

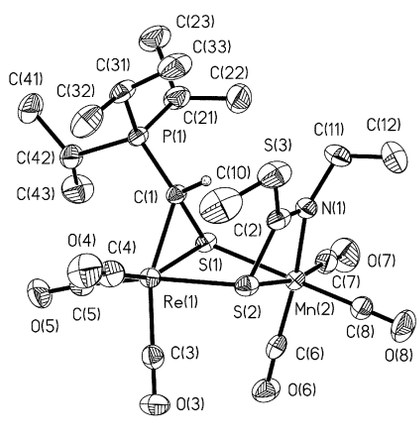
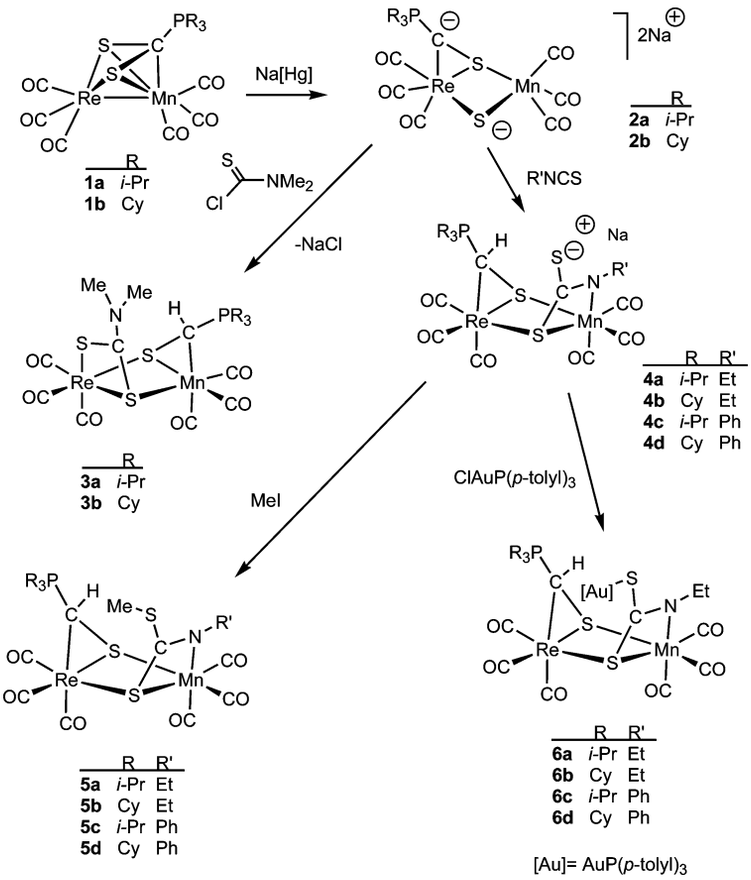


Fig. 2 Perspective view of the molecule of $[MnRe(CO)_6\{\mu\text{-}SCS(Me)NEt\}\{\mu\text{-}SC(H)PPr^i_3\}]$ (**5a**), showing the atom numbering.

The main features of the structures of **5a** (Fig. 2) and **5c** (Fig. 3) are consistent with those encountered in the structure



Scheme 1

Table 4 Selected interatomic distances (Å), and angles (°) in [MnRe(CO)$_6${μ-SCS(Me)NPh}{μ-SC(H)PPr$^i_3$}] (**5c**)

Re(1)–C(4)	1.876(9)	Re(1)–C(5)	1.890(8)
Re(1)–C(3)	1.916(8)	Re(1)–C(1)	2.219(6)
Re(1)–S(1)	2.4495(18)	Re(1)–S(2)	2.5581(18)
Mn(2)–C(7)	1.793(8)	Mn(2)–C(8)	1.797(8)
Mn(2)–C(6)	1.799(8)	Mn(2)–N(1)	2.094(5)
Mn(2)–S(1)	2.431(2)	Mn(2)–S(2)	2.4674(17)
S(1)–C(1)	1.820(6)	S(2)–C(9)	1.756(6)
P(1)–C(1)	1.763(6)	N(1)–C(9)	1.293(7)
N(1)–C(13)	1.429(7)	S(3)–C(9)	1.745(6)
S(3)–C(10)	1.789(7)		
C(5)–Re(1)–C(1)	115.2(3)	C(3)–Re(1)–C(1)	153.9(3)
C(4)–Re(1)–S(1)	101.8(2)	C(5)–Re(1)–S(1)	159.6(2)
C(3)–Re(1)–S(1)	108.6(2)	C(1)–Re(1)–S(1)	45.55(14)
C(4)–Re(1)–S(2)	173.4(2)	C(1)–Re(1)–S(2)	86.52(16)
S(1)–Re(1)–S(2)	81.21(6)	C(7)–Mn(2)–N(1)	100.1(2)
C(8)–Mn(2)–N(1)	89.6(3)	C(6)–Mn(2)–N(1)	166.6(2)
C(8)–Mn(2)–S(1)	177.8(2)	N(1)–Mn(2)–S(2)	66.65(13)
C(1)–S(1)–Mn(2)	111.7(2)	C(1)–S(1)–Re(1)	60.51(18)
Mn(2)–S(1)–Re(1)	96.86(7)	C(9)–S(2)–Mn(2)	78.13(19)
C(9)–S(2)–Re(1)	110.2(2)	Mn(2)–S(2)–Re(1)	93.17(6)
C(1)–P(1)–C(41)	113.8(3)	C(1)–P(1)–C(21)	106.7(3)
C(41)–P(1)–C(21)	106.5(4)	C(1)–P(1)–C(31)	110.5(4)
C(21)–P(1)–C(31)	106.2(4)	C(9)–N(1)–C(13)	124.1(5)
C(9)–N(1)–Mn(2)	104.3(4)	C(13)–N(1)–Mn(2)	131.1(4)
P(1)–C(1)–S(1)	116.7(3)	P(1)–C(1)–Re(1)	132.1(3)
S(1)–C(1)–Re(1)	73.9(2)	C(9)–S(3)–C(10)	102.2(3)
S(3)–C(9)–S(2)	124.3(3)		

of **3a**. Again there is protonation of the carbon atom to give a bridging $R_3PC(H)S^-$ ligand which is bonded as η^2(S,C) to rhenium and as η^1(S) to manganese. A new bridging methyldithiocarbimato ligand has been generated by electrophilic addition of the isothiocyanate to the bridging sulfur of the anion, followed by coordination of the nitrogen to manganese, and methylation of the terminal sulfur. However, there are some differences in the overall structures which deserve some

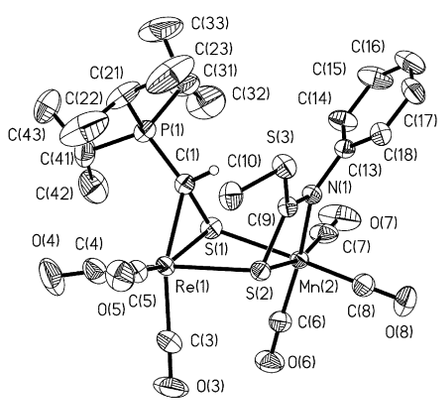


Fig. 3 Perspective view of the molecule of [MnRe(CO)$_6${μ-SCS(Me)NPh}{μ-SC(H)PPr$^i_3$}] (**5c**), showing the atom numbering.

comment. As it can be seen in **3a**, the carbon atom of the $R_3PC(H)S^-$ ligand is bonded to manganese, this being the only product of the reaction, according to the available spectroscopic data. In contrast, in the structures of **5a** and **5c**, the carbon atom is bonded to rhenium. We have previously found [4] that the protonation of heterobinuclear anions **2a** initially produces a complex with carbon bonded to Re (kinetic product), which subsequently isomerizes to the complex with carbon bonded to Mn (thermodynamic product). The isomerization seems to require the production of a coordination vacancy through ligand dissociation. In the case of complexes **3a**–**d** the isomerization seems to be complete while for **5a**–**d** it occurs only partially. In fact, for both structures **5a** and **5c**, it has been found that Mn and Re are disordered between the two metal sites. The final refinement for **5a** gave an occupancy factor ratio for Re : Mn of 0.72 : 0.28 for the metal bonded to carbon, which is labeled Re(1) in Fig. 2 (respectively 0.86 : 0.14 for **5c**). This is consistent with the appearance of two isomers in the

solution spectra of the crude reaction as mentioned above. Since there should not be great differences in the overall size and shape of the molecules of the two isomers, it is not surprising that both molecules can easily pack together in the same lattice, keeping approximately the same proportion as they occur in the solution. It is remarkable that the isomerization is complete in the formation of the dithiocarbamate **3a** while it is only incipient for complexes **5**. This suggests that the μ_2(S,N) coordination of the dithiocarbimato ligand in **4** or **5** is more difficult to dissociate than the μ_2(S,S) coordination of the dithiocarbamato ligand in **3**.

Another feature of interest in these reactions is the protonation of the carbon atom of the R_3PCS ligand. In the light of previous results, as summarized in Chart 1, it seems that the carbon atom is efficiently hindered by the bulky substituents of the phosphine and, in fact, it is only accessible to the proton. Even a methyl group is too big to attack the carbon, and the reaction of anionic **2a**–**b** with MeI produces a double methylation at sulfur.[5] On the other hand, dithiocarbamoyl chloride and isothiocyanate are hygroscopic and easily hydrolysed, therefore it is difficult to avoid traces of moisture and acid. A fast protonation of the carbon is likely to occur, followed by the electrophilic addition to the bridging sulfur. However, IR monitoring of the reaction mixture gives no information about a possible intermediate.

N-Ethyldithiocarbimate anions **4a**–**b** react with ClAuP(*p*-tolyl)$_3$ at low temperature (−78 °C) to afford neutral complexes **6a**–**b** (see Scheme 1) which were isolated as microcrystalline solids and characterised by analytical and spectroscopic methods (see Experimental). Unfortunately, it was not possible to obtain crystals suitable for X-ray determination. Nevertheless, the available spectroscopic data strongly suggest for complexes **6a**–**b** a structure analogous to that determined for complexes **5**, in which the electrophilic $AuPR_3$ fragment is added to the terminal sulfur. As with methylated complexes **5a**–**d** spectroscopic data in solution indicate the presence of two isomers which differ in the carbon being bonded to Re (Major isomer) or to Mn (minor isomer) The isomer ratio, as estimated from ^{31}P NMR spectra in solution is about the same obtained for the methylated complexes **5** (10 : 1). This indicates that the isomerization process takes place during the electrophilic addition of isothiocyanate to anions **2**, to produce **4a**–**d**. When ClAu(*p*-tolyl)$_3$ was made to react with *N*-phenyl dithiocarbimate anions **4c**–**d** extensive decomposition was observed, and it was not possible to isolate any stable product from the reaction mixtures.

In conclusion, we have demonstrated that it is possible to build selectively, within a heterobimetallic system, dithiocarbamato or dithiocarbimato complexes, the latter featuring an unprecedented bonding mode.

Experimental

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of the instrumentation and experimental procedures have been given elsewhere.[6] Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

[MnRe(CO)$_6$(μ-S$_2$CNMe$_2$){μ-SC(H)PPr$^i_3$}] (3a)

To a cooled (−78 °C) solution of **2a**[4] (0.15 mmol) in THF (20 ml) was added *N*,*N*-dimethylthiocarbamoyl chloride (0.019g, 0.15 mmol) and the mixture was allowed to warm slowly to room temperature, and then stirred for 3 h. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2–hexane (1 : 1, v/v, 3 × 15 ml) and the collected extracts were filtered through a short column of alumina (2.5 × 5 cm, activation degree III). The solvent was evaporated and the residue was washed several times with hexane. The resulting oily solid was dissolved in the minimum amount of CH_2Cl_2, and layered with hexane. Slow diffusion at −20 °C afforded compound **3a** as orange crystals. Yield 0.068 g, 61%. Anal. Calc. for $C_{19}H_{28}MnNO_6PReS_3$: C, 31.06; H, 3.84; N, 1.90. Found: C, 30.92; H, 3.82; N, 1.88%. IR (THF) *ν* (CO) 2019s, 1989vs, 1916s, 1902s, 1895s, 1877m cm^{-1}. ^{1}H NMR (CD_2Cl_2) *δ* 3.30 and 3.20 [2 s, 6H, N(C*H*$_3$)$_2$], 2.60 [m, (1 + 3)H, SC*H*P, and C*H* of PPr$^i_3$], 1.50 [m, 18H, C*H*$_3$ of PPr$^i_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2) *δ* 51.19. ^{13}C{^{1}H} NMR (CD_2Cl_2) 225.8 [a, 3 Mn*C*O], 210.5 [s, S$_2$*C*N], 195.6, 195.0, 190.7 [3 Re*C*O], 40.5 and 40.0 [2 s, N(*C*H$_3$)$_2$], 24.6 [d(45), *C*H of Pr^i], 18.1 [d (18), *C*H$_3$ of Pr^i].

[MnRe(CO)$_6$(μ-S$_2$CNMe$_2$){μ-SC(H)PCy$_3$}] (3b)

Compound **3b** was prepared as described for **3a** from a solution of **2b** (0.19 mmol) and *N*,*N*-dimethylthiocarbamoyl chloride (0.023 g, 0.19 mmol). Similar workup gave **3b** as orange crystals. Yield 0.11 g, 67%. Anal. Calc. for $C_{28}H_{40}MnNO_6PReS_3$: C, 39.34; H, 4.72; N, 1.64. Found: C, 39.38; H, 4.60; N, 1.65%. IR (THF) *ν* (CO) 2019s, 1989vs, 1915s, 1902s, 1894s, 1875m cm^{-1}. ^{1}H NMR (CD_2Cl_2) *δ* 3.31 and 3.22 [2 s, 6H, N(C*H*$_3$)$_2$], 2.64 [a, 1H, SC*H*P], 2.31 to 0.85 [m, 33H, C*H* and C*H*$_2$ of Cy]. ^{31}P{^{1}H} NMR (CD_2Cl_2) *δ* 41.69. ^{13}C{^{1}H} NMR (CD_2Cl_2) *δ* 226.6 [a, 3 Mn*C*O], 210.9 [s, S$_2$*C*N], 196.0, 195.4, 191.1 [3 Re*C*O], 40.7 and 40.4 [2 s, N(*C*H$_3$)$_2$], 34.6 [d(43), *C*^{1} of Cy], 28.3 and 27.3 [2 s, *C*^{2} and *C*^{6} of Cy], 27.3 and 26.8 [2 d(11), *C*^{3} and *C*^{5} of Cy], 26.1 [s, *C*^{4} of Cy].

Na[MnRe(CO)$_6$(μ-S$_2$CNEt){μ-SC(H)PPr$^i_3$}] (4a)

To a cooled (−78 °C) solution of **2a** (0.23 mmol) in THF (20 ml) was added ethylisothiocyanate (21 μl, 0.23 mmol) and the mixture was allowed to warm slowly to room temperature, and then stirred for 3 h. The resulting solution was used in subsequent reactions. IR (THF) *ν* (CO) 2007s, 1982vs, 1906sh, 1897s, 1877s, 1856s cm^{-1}.

Na[MnRe(CO)$_6$(μ-S$_2$CNEt){μ-SC(H)PCy$_3$}] (4b)

The preparation was as described for **4a**, from **2a** (0.19 mmol) and ethylisothiocyanate (16 μl, 0.19 mmol), to obtain a THF solution of **4b**. IR (THF) *ν* (CO) 2007s, 1981vs, 1908sh, 1898s, 1876s, 1854s cm^{-1}.

Na[MnRe(CO)$_6$(μ-S$_2$CNPh){μ-SC(H)PPr$^i_3$}] (4c)

The preparation was as described for **4a**, from **2b** (0.23 mmol) and phenylisothiocyanate (28 μl, 0.23 mmol), to obtain a THF solution of **4c**. IR (THF) *ν* (CO) 2010s, 1984vs, 1910sh, 1902s, 1880s, 1858s cm^{-1}.

Na[MnRe(CO)$_6$(μ-S$_2$CNPh){μ-SC(H)PCy$_3$}] (4d)

The preparation was as described for **4a**, from **2b** (0.13 mmol) and phenylisothiocyanate (16 μl, 0.23 mmol), to obtain a THF solution of **4c**. IR (THF) *ν* (CO) 2005s, 1981vs, 1900h, 1877s, 1854s cm^{-1}.

[MnRe(CO)$_6${μ-SCS(Me)NEt}{μ-SC(H)PPr$^i_3$}] (5a)

To a solution of **4a** (0.23 mmol) in THF (20 ml) was added MeI (15 μl, 0.23 mmol) and the mixture was stirred for 3 h. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2–hexane (1 : 2, v/v, 3 × 15 ml) and the collected extracts were filtered through a short column of alumina (2.5 × 5 cm, activation degree III). The solvent was evaporated *in vacuo* to give **5a** as orange crystals. Yield 0.105 g, 61%. Anal. Calc. for $C_{20}H_{30}MnNO_6PReS_3$: C, 32.01; H, 4.03; N, 1.87. Found: C, 32.14; H, 4.05; N, 1.83%. IR (THF) *ν* (CO) 2022s, 1994vs, 1929s, 1915s, 1893s, 1870s cm^{-1}. ^{1}H NMR (CD_2Cl_2) *δ* 3.92 and 3.50 [2 s, (1 + 1)H, C*H*$_2$ of EtNCS], 2.5 [m, (3 + 3)H, SC*H*$_3$ and C*H* of PPr$^i_3$], 1.42 [m, (1 + 3 + 18)H, SC*H*P, C*H*$_3$ of

Et, and CH_3 of PPr$^i_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 53.1 (minor isomer), 50.4 (Major isomer). ^{13}C{^{1}H} NMR (CD_2Cl_2) 230.5 and 223.7 [2 s, (1 + 2) Mn*C*O], 200.3, 199.6, and 197.0 [3 Re*C*O], 172.5 [s, EtN*C*S], 52.5 [s, *C*H$_2$ of EtNCS], 24.4 [d(45), *C*H of Pr^i], 18.2 [d (19), *C*H$_3$ of Pr^i], 14.4 [s, S*C*H$_3$], 14.3 [*C*H$_3$ of Et], 4.6 [d(37), S*C*HP].

[MnRe(CO)$_6${μ-SCS(Me)NEt}{μ-SC(H)PCy$_3$}] (5b)

Compound **5b** was prepared as described above for **5a** from **4b** (0.19 mmol) and MeI (12 μl, 0.19 mmol). Similar workup gave **5b** as orange crystals. Yield 0.085 g, 52%. Anal. Calc. for $C_{29}H_{42}MnNO_6PReS_3$: C, 40.08; H, 4.87; N, 1.61. Found: C, 39.73; H, 4.61; N, 1.59%. IR (THF) *ν* (CO) 2022s, 1994vs, 1930s, 1916s, 1893s, 1869s cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 3.90 and 3.52 [2 s, 2H, C*H*$_2$ of EtNCS], 2.5 to 0.7 [m, (1 + 3 + 3 + 33)H, SC*H*P, SC*H*$_3$, C*H*$_3$ of Et, C*H* and C*H*$_2$ of Cy]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 43.9 (m), 41.32 (M). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 223.2 and 218.1 [2 s, (1 + 2) Mn*C*O], 199.9, 199.6, and 196.7 [3 Re*C*O], 172.0 [s, EtN*C*S], 52.1 [s, *C*H$_2$ of EtNCS], 33.7 [d(43), *C*^{1} of Cy], 28.4 and 28.0 [2 s, *C*^{2} and *C*^{6} of Cy], 27.3 and 26.6 [2 d(11), *C*^{3} and *C*^{5} of Cy], 26.2 [s, *C*^{4} of Cy], 14.5 [s, S*C*H$_3$], 13.8 [s, *C*H$_3$ of Et], 6.0 [d(36), S*C*HP].

[MnRe(CO)$_6${μ-SCS(Me)NPh}{μ-SC(H)PPr$^i_3$}] (5c)

Compound **5b** was prepared as described above for **5a** from **4c** (0.23 mmol) and MeI (15 μl, 0.23 mmol). Similar workup gave **5c** as orange crystals. Yield 0.040 g, 22%. Anal. Calc. for $C_{24}H_{30}MnNO_6PReS_3$: C, 36.17; H, 3.79; N, 1.75. Found: C, 35.89; H, 3.79; N, 1.60%. IR (THF) *ν* (CO) 2025s, 1996vs, 1931s, 1920s, 1895s, 1872s cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.5 to 7.3 [m, 5H, C$_6$*H*$_5$], 2.5 [m, (3 + 3)H, SC*H*$_3$ and C*H* of PPr$^i_3$], 1.53 to 1.31 [m, (1 + 18)H, SC*H*P and C*H*$_3$ of PPr$^i_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 51.68 (m), 48.66 (M). ^{13}C{^{1}H} NMR (CD_2Cl_2) 225.0 223.2 [2 s, (1 + 2) Mn*C*O], 199.6, 199.4, and 197.1 [3 Re*C*O], 177.1 [s, PhN*C*S], 148.6 [s, *C*^{1} of Ph], 129.8 [s, *C*^{2} and *C*^{6} of Ph], 128.1 [s, *C*^{4} of Ph], 123.7 [s, *C*^{3} and *C*^{5} of Ph], 25.5 [d(44), *C*H of Pr^i], 18.5 [d (19), *C*H$_3$ of Pr^i], 15.2 [s, S*C*H$_3$], 5.4 [d(37), S*C*HP].

[MnRe(CO)$_6${μ-SCS(Me)NPh}{μ-SC(H)PCy$_3$}] (5d)

Compound **5d** was prepared as described above for **5a** from **4d** (0.13 mmol) and MeI (9 μl, 0.13 mmol). Similar workup gave **5d** as orange crystals. Yield 0.053 g, 45%. Anal. Calc. for $C_{33}H_{42}MnNO_6PReS_3$: C, 43.22; H, 4.61; N, 1.52. Found: C, 43.85; H, 4.70 N, 1.79%. IR (THF) *ν* (CO) 2023s, 1994vs, 1920s, 1895s, 1871s cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.47 [m, 5H, C$_6$*H*$_5$], 2.60 to 1.10 [m, (1 + 3 + 33)H, SC*H*P, SC*H*$_3$, C*H* and C*H*$_2$ of Cy]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 42.41 (m), 39.57 (M). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 223.7, 222.5, 218.0 [3 s, 3 Mn*C*O], 199.7, 199.2, and 197.3 [3 Re*C*O], 176.8 [s, PhN*C*S], 148.1 [s, *C*^{1} of Ph], 129.6 [s, *C*^{2} and *C*^{6} of Ph], 127.7 [s, *C*^{4} of Ph], 123.4 [s, *C*^{3} and *C*^{5} of Ph], 34.6 [d(42), *C*^{1} of Cy], 28.2 and 27.9 [2 s, *C*^{2} and *C*^{6} of Cy], 27.2 and 26.8 [2 d(11), *C*^{3} and *C*^{5} of Cy], 26.1 [s, *C*^{4} of Cy], 14.9 [s, S*C*H$_3$], 6.9 [d(36), S*C*HP].

[MnRe(CO)$_6${μ-SCS{AuP(*p*-tolyl)$_3$}NEt}{μ-SC(H)PPr$^i_3$}] (6a)

To a cooled (ice bath) solution of **4a** (0.23 mmol) in THF (20 ml) was added [AuClP(*p*-tolyl)$_3$] (0.123 g, 0.23 mmol) and the mixture was stirred for 15 min. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2–hexane (1 : 2, v/v, 3 × 15 ml) and the collected extracts were filtered through a short column of alumina (2.5 × 5 cm, activation degree III). The solvent was evaporated *in vacuo* to give **6a** as yellow microcrystals. Yield 0.090 g, 32%. Anal. Calc. for $C_{40}H_{48}AuMnNO_6P_2ReS_3$: C, 38.90; H, 3.91; N, 1.13. Found: C, 39.10; H, 4.08; N, 1.01%. IR (THF) *ν* (CO) 2015s, 1989vs, 1921s, 1907s, 1886s, 1862s cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.3 [m, 12H, C*H* of *p*-tolyl], 4.61 and 3.57 [2 s, (1 + 1)H, C*H*$_2$ of EtNCS], 2.34 [m, (3 + 9)H, C*H* of PPr$^i_3$ and C*H*$_3$ of *p*-tolyl], 1.45 [m, (1 + 3 + 18)H, SC*H*P, C*H*$_3$ of Et, and C*H*$_3$ of PPr$^i_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 53.2 (minor isomer), 50.7 (Major isomer) [s, SC(H)*P*], 35.4 [s, *P*(*p*-tolyl)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2) 223.5 [s, 3 Mn*C*O], 200.4, 200.0, and 197.7 [3 Re*C*O], 142.7 [s, *C*^{4} of *p*-tolyl], 134.4 [d(14), *C*^{2} and *C*^{6} of *p*-tolyl], 130.1 [d(11), *C*^{3} and *C*^{5} of *p*-tolyl], 126.6 [d(60), *C*^{1} of *p*-tolyl], 52.2 [s, *C*H$_2$ of EtNCS], 24.3 [d(45), *C*H of Pr^i], 21.6 [s, *C*H$_3$ of *p*-tolyl], 18.7 [d (19), *C*H$_3$ of Pr^i], 14.2 [*C*H$_3$ of Et], 5.3 [d(38), S*C*HP].

[MnRe(CO)$_6${μ-SCS{AuP(*p*-tolyl)$_3$}NEt}{μ-SC(H)PCy$_3$}] (6b)

Compound **6b** was prepared as described for **6a** from **5b** (0.19 mmol) and [AuClP(*p*-tolyl)$_3$] (0.107 g, 0.19 mmol). Similar workup gave **6b** as a yellow microcrystalline solid. [AuClP(*p*-tolyl)$_3$] (0.123 g, 0.23 mmol) and the mixture was stirred for 15 min. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2–hexane (1 : 2, v/v, 3 × 15 ml) and the collected extracts were filtered through a short column of alumina (2.5 × 5 cm, activation degree III). The solvent was evaporated *in vacuo* to give **6a** as yellow microcrystals. Yield 0.116g, 45%. Anal. Calc. for $C_{49}H_{60}AuMnNO_6P_2ReS_3$: C, 43.42; H, 4.46; N, 1.03. Found: C, 43.04; H, 4.77; N, 0.99%. IR (THF) *ν* (CO) 2015s, 1988vs, 1920s, 1907s, 1884s, 1862s cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.3 [m, 12H, C*H* of *p*-tolyl], 4.13 and 3.48 [2 s, (1 + 1)H, C*H*$_2$ of EtNCS], 2.34 to 0.97 [m, (1 + 3 + 9 + 3 + 33)H, SC*H*P, C*H*$_3$ of Et, C*H*$_3$ of *p*-tolyl, C*H* and C*H*$_2$ of Cy]. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 44.5 (m), 41.9 (M) [s, SC(H)*P*], 35.8 [s, *P*(*p*-tolyl)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2) 224.2, 223.5, and 219.7 [3 Mn*C*O], 200.5, 200.1, and 197.6 [3 Re*C*O], 178.3 [s, EtN*C*S], 142.6 [s, *C*^{4} of *p*-tolyl], 134.4 [d(14), *C*^{2} and *C*^{6} of *p*-tolyl], 130.1 [d(12), *C*^{3} and *C*^{5} of *p*-tolyl], 126.5 [d(61), *C*^{1} of *p*-tolyl], 52.3 [s, *C*H$_2$ of EtNCS], 33.8 [d(43), *C*^{1} of Cy], 28.5 and 28.0 [2 s, *C*^{2} and *C*^{6} of Cy], 27.5 and 26.7 [2 d(10), *C*^{3} and *C*^{5} of Cy], 26.2 [s, *C*^{4} of Cy], 20.6 [s, *C*H$_3$ of *p*-tolyl], 14.3 [*C*H$_3$ of Et], 6.9 [d(37), S*C*HP].

X-Ray diffraction study of 3a

Crystals were grown by slow diffusion of hexane into a concentrated solution of in THF at −20 °C. Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least squares refinement of a set of 25 centered reflections in the range $15 < \theta/° < 18$. Three reflections were measured every 1 h as orientation and intensity controls. Significant decay was not observed. The structure was solved by Patterson methods, phase expansion, and subsequent Fourier maps with DIRDIF.[7] Full-matrix least squares refinement was made with SHELX-93.[8] After isotropic refinement, an absorption correction was applied with DIFABS.[9] Most non-hydrogen atoms were refined anisotropically. The carbon atoms of two isopropyl groups of PPr$^i_3$ were affected by some incipient disorder which could not be satisfactorily modelled. The affected carbon atoms were kept isotropic, and the two isopropyls were refined as rigid groups, with constrained C–C distances. Hydrogen atoms were geometrically positioned, with a common isotropic temperature factor which was refined.

X-Ray diffraction study of 5a and 5c

Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH_2Cl_2 at −20 °C. Relevant crystallographic details are given in Table 1. Intensity measurement was made with a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[10] program. The structures were solved by direct methods with SHELXTL.[11] A semi-empirical absorption correction was applied with the program SADABS.[12] All non-hydrogen atoms were refined

anisotropically. The metal atoms were disordered between the two positions. The occupancy of each metal on each site was refined with the constraints EADP and EXYZ while keeping the total sum equal to unit for each site. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

CCDC reference numbers 208877 (**3a**), 208878 (**5a**) and 208879 (**5c**).

See http://www.rsc.org/suppdata/dt/b3/b304432g/ for crystallographic data in CIF or other electronic format.

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