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Dithiocarbamyl-substituted diphosphanylmethanide complexes of manganese(I): a new type of ambivalent metalloligands

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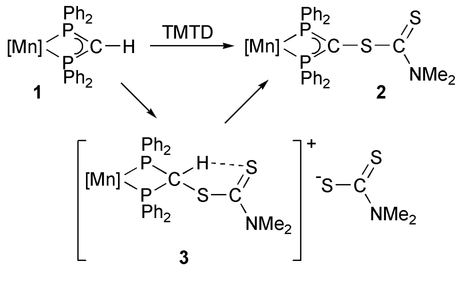
The diphosphanylmethanide complex $[Mn(CO)_4\{(PPh_2)_2C–H\}]$ promotes S–S bond breaking in tetramethylthiuram disulfide affording $[Mn(CO)_4\{(PPh_2)_2C–S–C(S)NMe_2\}]$ (2), which proved to be a valuable host for binding cations through the methanide carbon atom and the thiocarbonyl group, allowing the controlled synthesis of heterometallic compounds.

Metalloligands are useful species for the rational design of heterometallic complexes. Most known S-donor metalloligands contain simple thiolate groups[1] or polythioether macrocycles,[2] and they show not only suitability for the synthesis of heterometallic compounds but also promise for attractive potential applications, such as redox-responsive sensors for the binding of late metals and encapsulation.[3] Most of these S-donor metalloligands display no other donor atom apart from sulfur. In relation to this, we describe here a new approach for the controlled synthesis of heterometallic complexes by preparing a dithiocarbamyl-substituted diphosphanylmethanide manganese(I) complex, namely $[Mn(CO)_4\{(PPh_2)_2C–S–C(S)NMe_2\}]$ (**2**), which behaves as an ambivalent C- and S-donor metalloligand through the methanide carbon atom and the sulfur atom from the thiocarbonyl unit.[4]†

Reaction of $[Mn(CO)_4\{(PPh_2)_2C–H\}]$ (**1**)[5] with one equivalent of tetramethylthiuram disulfide (TMTD) in refluxing toluene produces a yellow solution of **2**. Crystals of **2** were obtained from CH_2Cl_2–hexane solutions in 70% yield, and were fully characterized, including a solid structure determination by X-ray analysis. As shown in Scheme 1, a mechanism can be proposed for this reaction involving heterolytic cleavage of the S–S bond[6] in TMTD affording the intermediate cationic complex **3** and dimethyldithiocarbamate anion, which further deprotonates **3** to give neutral **2**. In fact, independent experiments show that **2** can be easily protonated by HBF_4 producing stable **3**, and that this is readily deprotonated by treatment with sodium dimethyldithiocarbamate affording **2**. The structure of **2** (Fig. 1 (A)) shows the presence of the new dithiocarbamyldiphosphanylmethanide ligand bonded through the phosphorus atoms to manganese, completing with the four carbonyl groups the octahedral coordination around this metal ion.‡ The planes C(1)–S(1)–C(2)–S(2) and P(1)–C(1)–P(2) are roughly orthogonal to each other and the carbon atom C(1) makes the P(1)–P(2)–C(1)–S(1) skeleton slightly pyramidal toward the S(2) atom (the C(1) atom lies 0.19 Å out of the P(1)–S(1)–P(2) plane), so that the structure clearly shows the availability of the C(1) and S(2) donor atoms to trap cations in a chelating manner. One example could be considered the proton itself giving the above-mentioned complex **3**. In the ^1H NMR spectrum of **3** the resonance of the P_2CH hydrogen is noteworthy, consisting of a triplet ($^2J_{PH}$ = 13 Hz) strongly shifted down field (δ 8.53). Considering that in most known C-functionalized bis(diphenylphosphino)methane ligands this signal appears in the range of 5.5–6.5 ppm,[7] the existence of a intramolecular C–H···S hydrogen bond in **3** completing a pseudo five-membered heterocycle seems very likely.



Scheme 1 Synthesis of complex **2**. [Mn] = $Mn(CO)_4$.

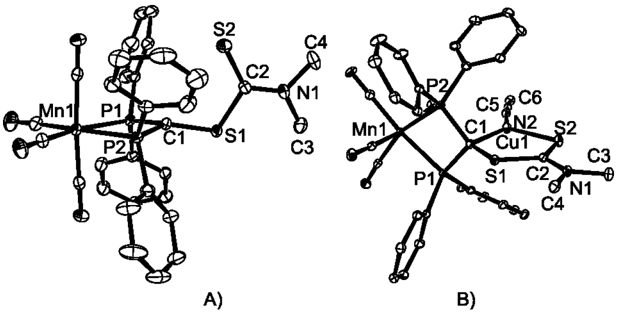
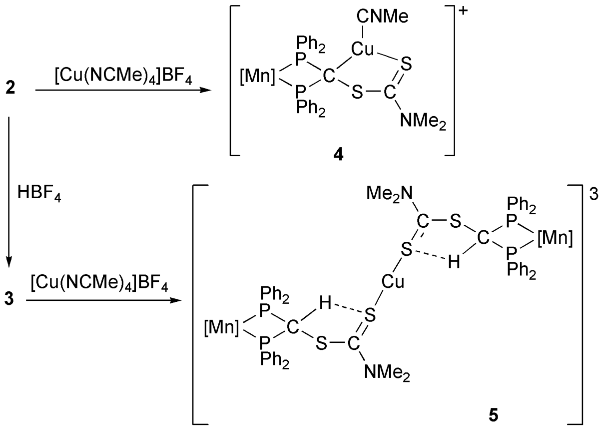


Fig. 1 ORTEP drawing of **2** (A) and **4** (B); hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: **2**: P(1)–C(1) 1.740(4), P(2)–C(1) 1.749(4), C(1)–S(1) 1.740(3), S(1)–C(2) 1.804(3), C(2)–S(2) 1.650(3), C(2)–N(1) 1.322(4); P(1)–C(1)–P(2) 100.79(17), C(1)–S(1)–C(2) 110.02(16). **4**: P(1)–C(1) 1.799(3), P(2)–C(1) 1.806(3), C(1)–S(1) 1.766(3), S(1)–C(2) 1.785(4), C(2)–S(2) 1.690(4), C(2)–N(1) 1.326(4), C(1)–Cu(1) 2.095(3), S(2)–Cu(1) 2.2317(9); P(1)–C(1)–P(2) 97.45(15), C(1)–S(1)–C(2) 108.91(16), C(1)–Cu(1)–S(2) 98.78, C(1)–Cu(1)–N(2) 138.91(12), S(2)–Cu(1)–N(2) 122.0(9).

Soft late metal ions are good candidates to be coordinated by metalloligand **2**. Thus, reaction of **2** with $[Cu(NCMe)_4]BF_4$ afforded, after a few minutes of stirring at room temperature, the heterometallic complex **4** (Scheme 2). The appreciable increase in the frequencies of the ν(CO) bands in the IR spectrum of **4** (2084, 2017, 2001, 1987 cm^{-1}) with respect to **2** (2074, 1996,



Scheme 2 Synthesis of complexes **4** and **5**. [Mn] = $Mn(CO)_4$.

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1963 cm^{-1}) gives a first indication that coordination through the methanide carbon atom has taken place. Apart from two methyl resonances corresponding to the dimethyldithiocarbamyl substituent (δ 3.49 and 3.57), the ^{1}H NMR spectrum of **4** shows a methyl signal (δ 1.86) in a zone indicative of coordinated acetonitrile. The structure of complex **4** was definitively established by X-ray crystallography. As shown in Fig. 1 (B) this complex displays a [Cu(NCMe)]$^+$ fragment bonded to C(1) and S(2) atoms to form a spirocyclic heterodimetallic cation. The five membered metallacycle C(1)–S(1)–C(2)–S(2)–Cu(1) is planar and orthogonal to the plane P(1)–C(1)–P(2). As expected, the P(1)–C(1) (1.799(3) Å) and P(2)–C(1) (1.806(3) Å) distances are longer than the corresponding distances in **2** (1.740(4) Å and 1.749(4) Å, respectively), as well as the C(2)–S(2) bond length (1.690(4) Å in **4** and 1.650(3) Å in **2**), owing to electron donation from C(1) and S(2) donor atoms to Cu(I).

The donor capability of **2** through the methanide carbon atom is disrupted on protonation, forming complex **3**, where the coordination ability is confined to the thiocarbonyl residue. Thus, treatment of **3** with half an equivalent of [Cu(NCMe)$_4$]BF$_4$ afforded the trimetallic cationic complex **5**, which displays ν(CO) bands in the IR spectrum at exactly the same frequencies than those of **3**, indicating that changes in the molecule have occurred far away from manganese. The P$_2$CH triplet in ^{1}H NMR spectrum of **5** has slightly changed (δ 8.26, $^2J_{PH}$ = 12 Hz) with respect to **3**, but still appears at very high chemical shift showing that the C–H$\cdots$S hydrogen bond still remains after coordination of the sulfur atom involved in such interactions. As we were unable to obtain suitable crystals of **5** for X-ray analysis, we prepared, by using the same synthetic approach as that for **5**, the very similar derivative *fac*-[Mn(CN-*t*-Bu)(CO)$_3${(PPh$_2$)$_2$C(H)SC(S)NMe$_2$}]$_2$Cu]$^{3+}$ (**5a**), in which a carbonyl ligand has been substituted by CN-*t*-Bu. The structure of **5a** (Fig. 2) shows the copper atom bridging two units of the manganese complex **3** through the thiocarbonyl sulfur atoms in a linear coordination mode. The structural data confirm the presence of two C–H$\cdots$S hydrogen bonds, as the S(2)–H(1) distance of 2.55(5) Å is clearly shorter than the sum of van der Waals radii of those atoms (3.15 Å).

The formation of **5** or **4** depending on whether the metalloligand **2** is protonated or not on the methanide carbon atom, and containing either linear or trigonal coordinated copper(I), respectively, suggests some relation of these species with pH dependent translocation of metal ions, a subject of great interest in supramolecular chemistry.[8]

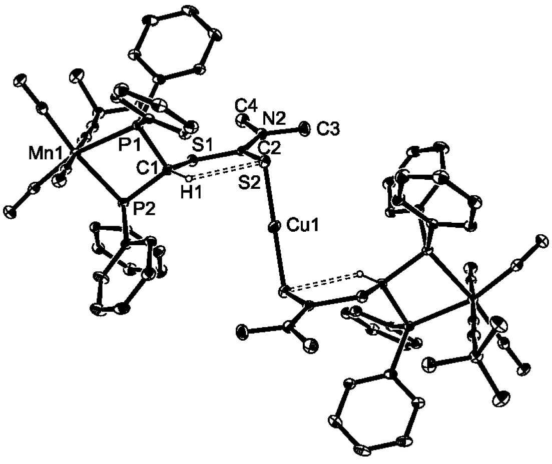

Fig. 2 ORTEP drawing of **5a**; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity. Selected bond distances [Å] and angles [°]: P(1)–C(1) 1.888(4), P(2)–C(1) 1.863(4), C(1)–S(1) 1.791(4), S(1)–C(2) 1.771(4), C(2)–S(2) 1.714(4), S(2)–Cu(1) 2.1639; P(1)–C(1)–P(2) 94.35(18), C(1)–S(1)–C(2) 104.37(18).

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Notes and references

† Selected spectroscopic data for **2**: IR (CH$_2$Cl$_2$), ν(CO) = 2074(s), 1996(vs), 1963(s) cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 3.30 (s, 6H, Me), 7.34–7.78 (20H, Ph); ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 20.0 (br). **3**: IR (CH$_2$Cl$_2$), ν(CO) = 2093(s), 2034(m), 2012(vs) cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 3.34 (s, 3H, Me), 3.46 (s, 3H, Me), 7.47–7.63 (20H, Ph), 8.53 (t, 1H, P$_2$CH); ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 48.4 (br). **4**: IR (CH$_2$Cl$_2$), ν(CO) = 2084(s), 2017(s), 2001(vs), 1987(s) cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 1.86 (s, 3H, Me), 3.49 (s, 3H, Me), 3.57 (s, 3H, Me), 7.48–7.70 (20H, Ph); ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 35.5 (br). **5**: IR (CH$_2$Cl$_2$), ν(CO) = 2093(s), 2034(m), 2012(vs) cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 3.42 (s, 3H, Me), 3.55 (s, 3H, Me), 7.49–7.68 (20H, Ph), 8.26 (t, 1H, P$_2$CH); ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 47.8 (br).

‡ *Crystal data* for **2** (C$_{32}$H$_{26}$MnNO$_4$P$_2$S$_2$): M = 669.54, crystal size 0.33 × 0.20 × 0.13 mm, a = 10.5648(7), b = 11.6965(6), c = 15.042(1) Å, α = 95.264(5), β = 104.315(4), γ = 115.24(4)°, V = 1587.3(6) Å^3, ρ_{calcd} = 1.401 g cm^{-3}, μ = 0.685 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 0.71073 Å, T = 293(2) K, θ_{max} = 25.98, independent reflections = 5620, refined parameters = 474, $R1$ = 0.0397, $wR2$ = 0.0902, largest diff. peak and hole 0.259 and −0.231 e Å^{-3}. CCDC 210265.

Crystal data for **4** ((C$_{34}$H$_{29}$CuMnN$_2$O$_4$P$_2$S$_2$)(BF$_4$).2(CH$_2$Cl$_2$)): M = 1030.79, crystal size 0.35 × 0.23 × 0.18 mm, a = 10.3689(1), b = 12.9100(2), c = 16.8117(2) Å, α = 101.757(1), β = 99.022(1), γ = 93.981(1)°, V = 2163.99(5) Å^3, ρ_{calcd} = 1.582 g cm^{-3}, μ = 7.355 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 1.5418 Å, T = 293(2) K, θ_{max} = 68.61, independent reflections = 7930, refined parameters = 638, $R1$ = 0.0546, $wR2$ = 0.1427, largest diff. peak and hole 1.151 and −0.799 e Å^{-3}. CCDC 210266.

Crystal data for **5a** ((C$_{72}$H$_{72}$CuMn$_2$N$_4$O$_6$P$_4$S$_4$)3(BF$_4$).2(CH$_2$Cl$_2$)): M = 1945.16, crystal size 0.08 × 0.05 × 0.03 mm, a = 11.1163(3), b = 19.3279(8), c = 21.773(1) Å, α = 69.660(3), β = 79.268(3), γ = 84.282(2)°, V = 4306.5(3) Å^3, ρ_{calcd} = 1.500 g cm^{-3}, μ = 6.054 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 1.5418 Å, T = 293(2) K, θ_{max} = 68.35, independent reflections = 15758, refined parameters = 1224, $R1$ = 0.0560, $wR2$ = 0.1375, largest diff. peak near to the solvent region and hole 2.170 and −0.893 e Å^{-3}. CCDC 210267.

See http://www.rsc.org/suppdata/cc/b3/b305045a/ for crystallographic data in .cif format.

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