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$[Mn_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]^{2-}$(*Mn*=*Mn*), a Nucleophilic Unsaturated Binuclear Anion

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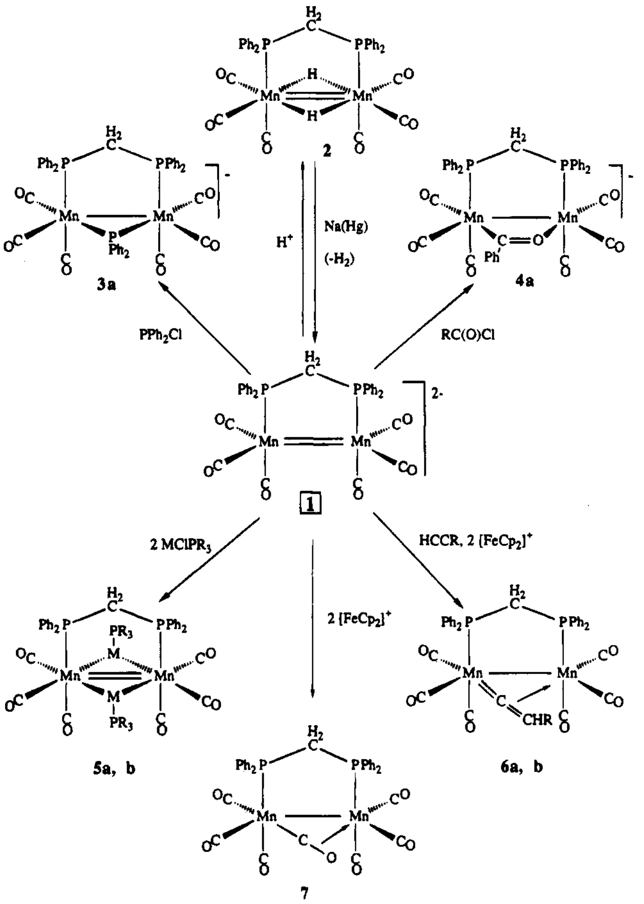
Summary: The dianionic complex $[Mn_2(CO)_6(\mu\text{-dppm})]^{2-}$ *(1) (dppm = $Ph_2PCH_2PPh_2$) is formed quantitatively as its Na^+ salt through the reaction of $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ and Na–amalgam in tetrahydrofuran. The wide chemistry of this nucleophilic anion is illustrated through its reactions with $PClPh_2$, PhC(O)Cl, $[MCl(PR_3)]$ (M = Ag, Au), and $[Fe(C_5H_5)_2][PF_6]$, all of them proceeding cleanly at low temperature.*

Transition-metal carbonyl anions are quite useful reagents in organometallic synthesis.[1] Although a large number of mononuclear and polynuclear species are known, the number of metal–metal bonded binuclear anions is comparatively low, and only a few of them have a negative charge larger than 1. Examples of the latter are, for example, $[Fe_2(CO)_8]^{2-}$,[2] $[M_2(\mu\text{-}H)_2(CO)_8]^{2-}$,[3] $[M_2(CO)_{10}]^{2-}$,[4] or the mixed-metal species $[FeM(CO)_9]^{2-}$ [4] (M = Cr, Mo, W). Apparently, there are not related group 7 transition-metal carbonylates available.[5] In this paper we report the synthesis of the very reactive dianion $[Mn_2(CO)_6(\mu\text{-dppm})]^{2-}$ (**1**) (Na^+ salt; dppm = $Ph_2PCH_2PPh_2$), a dppm-stabilized derivative of the yet unknown $[Mn_2(CO)_8]^{2-}$(*Mn*=*Mn*) anion.[6] The combination of a dinegative charge with the presence of a formally double metal–metal bond in compound **1** provides this anion with a remarkably wide synthetic potential, as illustrated by the reactions shown in Scheme 1.

Scheme 1



Anion **1** (Na^+ salt) is nearly quantitatively prepared by chemical reduction of the unsaturated dihydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (**2**)[7] with Na amalgam at room temperature, as revealed by IR and NMR analysis of the reaction mixture.[8] Attempts to isolate this air and moisture-sensitive green complex as a crystalline solid have been unsuccessful so far, but filtration of the reaction mixture under nitrogen gives a deep green solution ready for further reactivity studies. As expected, anion **1** reacts readily with $[NH_4][PF_6]$ to regenerate dihydride **2**.

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[1] Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1 and references therein.

[2] Hieber, W.; Beck, W.; Braun, G. *Angew. Chem.* **1960**, *72*, 795.

[3] Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

[4] Behrens, H. *Adv. Organomet. Chem.* **1980**, *18*, 1 and references therein.

[5] To our knowledge, the first group 7 metal carbonylate within this class is $[Mn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{:}\eta^2\text{-}OP(OEt)_2\}(CO)_6]^{2-}$, recently characterized in our laboratory: Liu, X.-Y.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1994**, *13*, 1940.

[6] The electronic structure of this hypothetical species, assuming a geometry related to that proposed for **1**, has been the subject of theoretical calculations. See: Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.

[7] García Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1992**, *11*, 370.

[8] All manipulations carried out under a nitrogen atmosphere using standard Schlenk techniques and carefully dried solvents. General conditions for NMR data: spectra recorded at 20 °C in CD_2Cl_2 solution, unless otherwise stated; chemical shifts (δ) in ppm relative to internal TMS [^1H at 300.13 MHz and ^{13}C (proton decoupled) at 75.47 MHz] or external 85% aqueous H_3PO_4 [^{31}P (proton decoupled) at 121.49 MHz]; coupling constants (J) in hertz. Preparation of THF solutions of **1**: In a typical experiment, *ca.* 1 mL of 0.7% Na–amalgam was added to a Schlenk flask containing complex **2** (0.066 g, 0.1 mmol) in THF (15 mL). The mixture was stirred at room temperature for 30 min, giving a dark green solution. The latter was filtered with a cannula and was ready for further use. Spectroscopic data for **1**: IR ν(CO) (cm^{-1}, THF) 1888 (s), 1841 (vs), 1817 (s), 1787 (s); ^{31}P NMR [THF/C_6D_6 (9/1)] δ 67.0 (s). The ^1H NMR spectrum of THF solutions of **1** showed no resonances in the region $\delta < 0$ ppm.

[9] Preparation of THF solutions of compounds **3a** and **4a**: A THF solution containing 0.1 mmol of **1** was treated with 18 μL of $PClPh_2$ (for **3a**) or 12 μL of PhC(O)Cl (for **4a**) at −78 °C. The solution turned red immediately and then was allowed to reach room temperature (*ca.* 15 min) and further stirred for 10 or 30 min, respectively. IR and ^{31}P NMR monitoring indicated in each case clean and complete formation of the title anions. Compound **3a**: ν(CO) (THF) 1972 (m), 1920 (s), 1891 (vs), 1842 (m), 1831 (m), 1800 (w); ^{31}P NMR [THF/C_6D_6 (9/1)] δ 209.3 (br, μ-PPh_2), 73.4 (br, μ-dppm). Compound **4a**: IR ν(CO) (THF) 1962 (s), 1900 (vs), 1870 (s), 1845 (m), 1835 (m, sh); ^{31}P NMR (THF) δ 65.2 (d, J_{PP} = 98), 55.9 (d, J_{PP} = 98).

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The presence of the dinegative charge and the relatively poor acceptor dppm ligand makes anion **1** a good nucleophile, in spite of the formal unsaturation of the molecule. Thus, complex **1** fails to react with CO, but displaces chloride easily from molecules such as $PClPh_2$ or PhC(O)Cl to give the novel orange anions $[Mn_2(\mu\text{-X})(CO)_6(\mu\text{-dppm})]^-$ (**3a**, **4a**) [**3a**, X = PPh_2; **4a**, X = η^2-C(Ph)O][9] in nearly quantitative yield (Scheme 1). The latter reactions resemble those reported[10] for the also unsaturated anion $[Fe_2(\mu\text{-}PPh_2)(CO)_6]^-$ which, however, seems to have a lower basicity, as indicated by the fact that it reacts with CO, in contrast with that observed for **1**. Protonation of anions **3a** or **4a** with $[NH_4][PF_6]$ gives the corresponding neutral hydrides $[Mn_2(\mu\text{-H})(\mu\text{-X})(CO)_6(\mu\text{-dppm})]$ (**3b**, **4b**)[11] in high yield. We note here that compound **3b** can be synthesized also from **2** and $PHPh_2$, but this reaction gives only small amounts (5%) of the complex.[12]

The presence of the manganese—manganese double bond in **1**, on the other hand, allows the synthesis of unsaturated mixed-metal clusters not accessible through other routes. Thus, the blue clusters $[Mn_2\{\mu\text{-M}(PR_3)\}_2(CO)_6(\mu\text{-dppm})]$ (**5a**,**b**) [**5a** M = Ag, R = C_6H_{11}; **5b** M = Au, R = *p*-tol][13] can be prepared in high yield through the reaction of **1** with the corresponding $[MCl(PR_3)]$ complexes (Scheme 1). The structure of **5b** has been confirmed by an X-ray diffraction study.[14]

A different reactivity at the dimanganese center can be induced by chemical oxidation of **1** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ at −78 °C. This gives a thermally unstable orange solution (thought to contain the solvated species $[Mn_2(CO)_6(THF)_2(\mu\text{-dppm})]$), which in fact acts as a source of the highly unsaturated "$Mn_2(CO)_6(\mu\text{-dppm})$" moiety. For example, addition of 1-alkynes (HCCR) to this solution and warming of the mixture to room temperature give the corresponding vinylidene complexes $[Mn_2(\mu{:}\eta^1,\eta^2\text{-C=CHR})(CO)_6(\mu\text{-dppm})]$ (**6a**,**b**) [**a**; R = Ph; **b**, R = ${}^tBu$] in yields higher than 80% within a few minutes.[15] This dramatically improves our previous synthesis for these complexes from **2** or $[Mn_2(CO)_8(\mu\text{-dppm})]$ and 1-alkynes, the latter reactions giving substantially lower yields (<40%) and requiring much longer reaction times.[7] On the other hand, thermal decomposition (20 °C) of the above mentioned orange solution gives the new heptacarbonylic complex $[Mn_2(\mu{:}\eta^1,\eta^2\text{-CO})(CO)_6(\mu\text{-dppm})]$ (**7**), which can be isolated as a moderately stable yellow solid.[16] Compound **7** is closely related to $[Mn_2(\mu{:}\eta^1,\eta^2\text{-CO})(CO)_8]$, an unstable species detected during different photolysis studies carried out on $[Mn_2(CO)_{10}]$,[17] and to $[Mn_2(\mu{:}\eta^1,\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$.[18,19] Complex **7** decomposes slowly (instantaneously in the presence of CO) in solution at room temperature to yield $[Mn_2(CO)_8(\mu\text{-dppm})]$,[18] a behavior that can be justified on steric grounds.[20] Obviously, the very mild conditions under which **7** can be formed from **1** are critical for its successful preparation.

The reactions of dianion **1** reported here show that this species is a highly versatile reagent for the syn-

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(10) Seyferth, D.; Brewer, K. S.; Wood, T. G.; Cowie, M.; Hilts, R. W. *Organometallics* **1992**, *11*, 2570.

(11) Preparation of **3b**: Excess $[NH_4][PF_6]$ was added to a THF solution containing 0.1 mmol of **3a** (prepared as described above and cooled at −78 °C), and the mixture was allowed to reach room temperature (*ca.* 15 min) and further stirred for 15 min to give a yellow solution. The solvent was removed under vacuum and the residue extracted with toluene and filtered. Crystallization of the filtrate from toluene−petroleum ether at −20 °C gave complex **3b** as a yellow microcrystalline solid (0.070 g, 83%). Spectroscopic data for this compound were identical to those described previously (see text and ref 12). Preparation of **4b**: Anion **4a** was protonated as described for **3a** to give a yellow solution. The solvent was then removed and the residue extracted with dichloromethane and chromatographed on alumina (activity III) at −40 °C. Elution with a dichloromethane−petroleum ether mixture (1:3) gave a yellow fraction which yielded, after removal of solvents in vacuum, complex **4b** as a yellow microcrystalline solid (0.054 g, 70%). Anal. Calcd for $C_{38}H_{28}Mn_2O_7P_2$: C, 59.39; H, 3.67. Found: C, 59.02; H, 3.55. IR, ν(CO) (CH_2Cl_2): 2030 (vs), 2001 (s) 1952 (s), 1931 (m, sh), 1913 (s). ${}^{31}P$ NMR: δ 54.9 (d, J_{PP} = 56), 45.2 (broad d, J_{PP} = 56). ${}^1H$ NMR: δ 7.5−6.9 (m, 25H, Ph), 3.11 (dt, $J_{HH} = J_{PH}$ = 13, 1H, CH_2), 2.43 (dt, J_{HH} = 13, J_{PH} = 10, 1H, CH_2), −16.56 (dd, J_{PH} = 30, 21, 1H, μ-H). ${}^{13}C$ NMR: δ 312.1 (d, J_{PC} = 20, μ-*C*(O)Ph), 223.0, 218.4, 217.3 (3 × m, 3 × MnCO), 222.5 (d, J_{PC} = 22, MnCO), 220.0 (d, J_{PC} = 14, MnCO), 219.8 (d, J_{PC} = 7, MnCO), 151.2 (s, C^1[PhC(O)]), 138.5−128.7 (complex, Ph), 29.5 (dd, J_{PC} = 18, 9, CH_2).

(12) Carreño, R.; Riera, V.; Ruiz, M. A. *J. Organomet. Chem.* **1991**, *419*, 163.

(13) Preparation of **5a**: Solid $AgCl\{P(C_6H_{11})_3\}$ (0.045 g, 0.106 mmol) was added to a THF solution containing 0.053 mmol of **1** at −78 °C. The solution turned blue rapidly and was then allowed to reach room temperature (*ca.* 15 min) and further stirred for 10 min. The solvent was then removed in vacuum and the residue extracted with dichloromethane−petroleum ether (1:2) and chromatographed on alumina (activity III) at −20 °C. Elution with dichloromethane−petroleum ether (1:3) gave a blue-violet fraction which yielded, after removal of solvents in vacuum, compound **5a** as a blue-violet microcrystalline solid (0.052 g, 69%). Anal. Calcd for $C_{67}H_{88}Ag_2Mn_2O_6P_4$: C, 55.92; H, 6.18. Found: C, 55.52; H, 5.93. IR, ν(CO) (CH_2Cl_2): 1954 (s), 1910 (vs), 1876 (m), 1850 (s). ${}^{31}P$ NMR (−60 °C): δ 73.05 (t of t, J_{PAg} = 16, J_{PP} = 6, Mn−P), 29.23 (2 × d of t, $J_{P^{109}Ag}$ = 358, $J_{P^{107}Ag}$ = 311, J_{PP} = 6, Ag−P). ${}^1H$ NMR (−60 °C): δ 7.7−7.1 (m, 20H, Ph), 5.24 (t, J_{PH} = 8, 2H, PCH_2), 1.80−1.24 (complex, 66H, C_6H_{11}). Preparation of **5b**: Solid $AuCl\{P(p\text{-tol})_3\}$ (0.061 g, 0.112 mmol) was added to a THF solution containing 0.056 mmol of **1** at −78 °C. The solution turned blue rapidly and was then allowed to reach room temperature (*ca.* 15 min) and further stirred for 10 min. Workup as described for **5a** yielded compound **5b** as a blue microcrystalline solid (0.067 g, 72%). Anal. Calcd for $C_{73}H_{64}Au_2Mn_2O_6P_4$: C, 52.66; H, 3.88. Found: C, 52.27; H, 3.87. IR, ν(CO) (CH_2Cl_2): 1972 (s), 1936 (vs), 1899 (m), 1871 (s). ${}^{31}P$ NMR: δ 69.2 (br, Mn−P), 65.7 (t, J_{PP} = 14, Au−P). ${}^1H$ NMR (−60 °C): δ 7.70 (m, 8H, Ph), 7.30−7.10 (complex, 28H, Ph and *p*-tol), 6.95 (t, J_{HH} = 6, 8H, Ph), 4.88 (t, J_{PH} = 10, 2H, PCH_2), 2.40 (s, 18H, Me).

(14) Tiripicchio, A.; Tiripicchio-Camellini, M. Unpublished results.

(15) Preparation of complexes **6a**,**b**: Excess HCCR (ca. 1 mL; **a**, R = Ph; **b**, R = ${}^tBu$) and $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$ (0.033 g, 0.1 mmol) were added to a solution containing 0.05 mmol of **1** at −78 °C. The mixture was then allowed to reach room temperature (*ca.* 15 min) and further stirred for 10 min to give a red-orange solution. The resulting vinylidene complexes (**6a** 0.033 g, 85%; **6b** 0.030 g, 80%) were isolated from the reaction mixtures as described previously (see ref 7).

(16) Preparation of **7**: Solid $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$ (0.033 g, 0.1 mmol) was added to a THF solution containing 0.05 mmol of **1** at −78 °C. The mixture turned orange rapidly and was then allowed to reach room temperature and further stirred for 30 min to give a yellow-orange solution. Solvent was then removed under vacuum and the residue extracted with toluene and filtered. Removal of solvent from the filtrate under vacuum and washing of the residue with petroleum ether (4 × 8 mL) at 0 °C yielded compound **7** as an analytically pure yellow powder (0.021 g, 61%). Anal. Calcd for $C_{32}H_{22}Mn_2O_7P_2$: C, 55.66; H, 3.22. Found: C, 55.92; H, 3.21. IR, ν(CO) (toluene): 2035 (vs), 1989 (s), 1964 (s), 1937 (m, sh), 1924 (s), 1900 (m, sh), 1708 (w). ${}^{31}P$ NMR: δ 68.2 (d, J_{PP} = 91), 51.8 (d, J_{PP} = 91). ${}^1H$ NMR: δ 7.6−7.0 (m, 20H, Ph), 3.36 (t, J_{PH} = 11, 2H, PCH_2). ${}^{13}C$ NMR (THF/C_6D_6 [9/1]): δ 233.2 (br, 2 × MnCO), 226.0 (br, 2 × MnCO), 223.6 (d, J_{PC} = 7, MnCO), 222.8 (d, J_{PC} = 26, MnCO), 215.3 (d, J_{PC} = 29, MnCO), 135.0−128.5 (Ph), 39.6 (t, J_{PC} = 19, CH_2). ${}^{13}C$ NMR [THF/C_6D_6, (9/1), −50 °C]: δ (Mn−CO) 239.0, 231.3, 227.5 (3 × m), 223.8 (s), 222.7 (d, J_{PC} = 27), 220.0 (m), 215.4 (d, J_{PC} = 29).

(17) (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Dunkin, I. A.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248. (c) Church, S. P.; Hermann, H.; Grevels, F.-G.; Shaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785. (d) Zhang, S.; Zhang, H.-T.; Brown, T. L. *Organometallics* **1992**, *12*, 3929.

(18) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673.

(19) Colton, R.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663.

(20) Studies on related $[Mn_2(CO)_x(\mu\text{-}R_2PCH_2PR_2)_2]$ complexes (x = 5 or 6) have suggested that the pentacarbonylic structures (containing the $\mu{:}\eta^1,\eta^2$ ligand) are more favored for the diphosphines having higher steric demands. See: Wolff, T. E.; Klemann, L. P. *Organometallics* **1982**, *1*, 1667. Therefore, one would predict a strong destabilization in the series $[Mn_2(\mu{:}\eta^1,\eta^2\text{-CO})(CO)_{8-2n}(\mu\text{-dppm})_n]$ as we proceed from $n = 2$ to $n = 0$.

thesis of new dimanganese carbonyl complexes. Further studies on the synthetic uses of **1**, mainly directed toward the formation of new manganese—carbon bonds under conditions of electronic unsaturation at the dimetal center, are in progress currently in our laboratory.

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