graphy (EtOAc/MeOH 4/1, then MeOH) to give **4** as a colorless solid (243 mg, 0.75 mmol) in 86 % yield.

Preparation of 9-*epi*-bromoquinine (**2**): Quinine **1**, PPh_3 (2 equiv) CBr_4 (1.1 equiv) were stirred in toluene at RT for 12 h. Workup by extraction with dilute hydrochloric acid, neutralization of aqueous extract (sat. $NaHCO_3$ solution) and back-extraction with $CHCl_3$ (ca. 5 ×). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography (EtOAc, then EtOAc/MeOH 4/1) gave **2**, colorless solid, yield 80 % (X-ray structure data in ref. [7]).

Crystal structure analysis of 9-epiquinine mesylate (**5**):[17] $C_{21}H_{26}N_2O_4S_1$, $M_r = 402.51$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.408(1)$, $b = 9.950(2)$, $c = 23.954(3)$ Å, $V = 2004.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.334\ g\,cm^{-3}$, $F(000) = 856$, crystal size $0.48 \times 0.14 \times 0.20$ mm, $T = 300$ K, $\mu(Mo_{K\alpha}) = 1.9\ cm^{-1}$. Data collection: Stoe IPDS diffractometer, graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 2Θ range $= 3.4-41.7°$, data set h, k, l $-8{:}8$; $-9{:}9$; $-23{:}23$, 7204 measured reflections, 2084 independent reflections, 1351 observed reflections with $I > 2\sigma(I)$, $R_{int} = 0.0945$. Structure solution with SHELXS-86 and refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, max./min. residual electron density $0.22/-0.23\ e\,Å^{-3}$, $R(F^1) = 0.0482$ based on 1351 reflections with $F_o > 4\sigma(F_o)$, $wR2 = 0.0814$, $wR2$ based on F^2 with 2084 reflections, Flack parameter $-0.1(2)$.

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[1] a) J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, pp. 292–307; b) F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, 4th ed., Plenum Press, New York, **1993**; c) A. Streitwieser *Chem. Rev.* **1956**, *56*, 571; A. Streitwieser, *Solvolytic Displacement Reactions*, McGraw–Hill, New York, **1962**; d) R. Brückner, *Reaktionsmechanismen*, Spektrum, Heidelberg, **1996**, p. 56.

[2] Naturally occurring carboxylic acids other than tartaric acid were also investigated, but gave some minor side products. The order of decreasing selectivity was: tartaric acid > malic acid, succinic acid, citric acid > mandelic acid > lactic acid, *p*-toluenesulfonic acid, sulfuric acid.

[3] See also: J. Susko, F. Szelag, *Bull. Int. Acad. Pol. Sci. Lett. Cl. Sci. Math. Nat. Ser. A* **1936**, 403.

[4] Thin layer chromatography was performed on silica gel plates (60 F_{254}, Merck). Detection with UV light and bromocresol green and purification by columm cromatography on silica gel showed no product other than 9-epiquinine (**4**). Diastereomeric quinine (**1**) was never observed.

[5] a) T. G. Waddell, T. Rambalakos, K. R. Christie, *J. Org. Chem.* **1990**, *55*, 4765; b) H. M. R. Hoffmann, O. Schrake, *Tetrahedron: Asymmetry* **1998**, *9*, 1051.

[6] a) J. Cossy, C. Dumas, D. G. Pardo, *Eur. J. Org. Chem.* **1999**, 1693; further recent examples: b) J. Wilken, M. Kossenjans, W. Saak, D. Haase, S. Pohl, J. Martens, *Liebigs Ann.* **1997**, 573.

[7] W. M. Braje, R. Wartchow, H. M. R. Hoffmann, *Angew. Chem.* **1999**, *111*, 2698; *Angew. Chem. Int. Ed.* **1999**, *38*, 2540.

[8] With neutral water as a solvent, 9-epibromoquinine (**2**) and silver benzoate also yield 9-epiquinine (**4**) as the only product with complete retention of configuration. However, the 1-azabicyclo[3.2.2] skeletal rearrangement[7] is strongly solvent dependent. This ring expansion involves fission of two σ-bonds and takes place, for example, with silver benzoate in methanol or with silver benzoate in anhydrous acetone.

[9] For a definition of *syn*, *anti* and *open*, *closed* conformations, see: a) G. D. H. Dijkstra, R. M. Kellogg, H. Wynberg, J. S. Svendsen, I. Markó, K. B. Sharpless, *J. Am. Chem. Soc.* **1989**, *111*, 8069; b) G. D. H. Dijkstra, R. M. Kellogg, H. Wynberg, *J. Org. Chem.* **1990**, *55*, 6121.

[10] See also: H. B. Bürgi, J. D. Dunitz, J. M. Lehn, G. Wipff, *Tetrahedron* **1974**, *30*, 1563.

[11] The conformation of 9-epiquinine mesylate (**5**) and 9-epibromoquinine (**2**)[7] was determined in the solid state (X-ray crystallography[17]) as well as in solution (NOE studies, solvent $CDCl_3$) as *syn*, *open* (Figure 1 b).

[12] Generation of a stabilized intermediate carbocation seems facile, because the π electron cloud of the quinoline moiety is oriented correctly for overlap with the vacant p orbital at C9 (Figure 1 b). Hydration of the (protonated) bridgehead nitrogen and of the leaving group in the *syn*, *open* conformation is thought to favor nucleophilic attack of the carbocation from the front. Nonetheless, since the intermediate cation is delocalized and comparatively long-lived, the stereochemical outcome, that is complete retention of configuration, is remarkable.

[13] 1-Phenylethyl halides (PhCH(Me)−X; X = Cl, Br), which may be considered as models for our O-mesyl cinchonanes and **2**, have been reported to solvolyse in aqueous ethanol with substantial racemization and up to 27 % inversion of configuration. See: C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., Cornell University Press, Ithaca, **1969**, p. 521, Table 33–1.

[14] X-ray crystal structure of the protonated quinine tartrate hemihydrate and conformation of the hydrogen tartrate ion: C. Ryttersgaard, S. Larsen, *Acta Crystallogr. Sect. C* **1998**, *54*, 1698.

[15] Selected recent examples for applications in asymmetric catalysis: Asymmetric dihydroxylation: a) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483; b) ion-pairing and asymmetric phase transfer catalysis: E. J. Corey, F.-Y. Zhang, *Angew. Chem.* **1999**, *111*, 2057; *Angew. Chem. Int. Ed.* **1999**, *38*, 1931; c) B. Lygo, J. Crosby, J. A. Peterson, *Tetrahedron Lett.* **1999**, *40*, 8671; d) M. J. O'Donnell, F. Delgado, R. S. Pottorf, *Tetrahedron* **1999**, *55*, 6347; e) D. Martyres, *Synlett* **1999**, *9*, 1508, and references therein.

[16] Further recent works in the field of *Cinchona* alkaloids: a) W. M. Braje, J. Frackenpohl, O. Schrake, R. Wartchow, W. Beil, H. M. R. Hoffmann, *Helv. Chim. Acta* **2000**, *83*, 777; b) S. Röper, J. Frackenpohl, O. Schrake, R. Wartchow, H. M. R. Hoffmann, *Org. Lett.* **2000**, *2*, in press; c) J. Frackenpohl, H. M. R. Hoffmann, *J. Org. Chem.* **2000**, *65*, in press.

[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-115799 (**5**) and -115802 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

P_6 Manganocene and P_3 Cymantrene: Consequences of the Inclusion of Phosphorus Atoms in Mn-Coordinated Cyclopentadienyl Ligands[**]

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Dedicated to Professor Karl-Heinz Thiele on the occasion of his 70th birthday.

The phosphorus-rich analogue of the cyclopentadienyl ligand 3,5-di(*tert*-butyl)-1,2,4-triphospholyl (**1**) can either be

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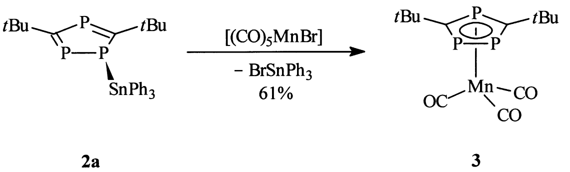
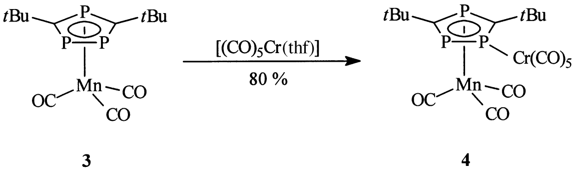
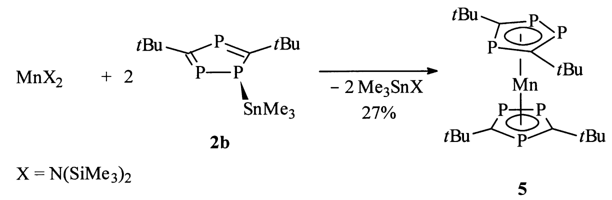
prepared from *tert*-butylphosphaalkyne units coordinated to a transition metal[1] or transferred to a metal center as the triphospholyl ion $\mathbf{1}^-$.[2] Both synthetic routes, however, lead to only poor yields of sandwich complexes with this ligand, so we prepared 1-triorganylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphole (**2**) as an alternative reagent for the transfer of **1** to a metal center.[3] As preliminary experiments, in which **2** was treated with cobalt(I) and tin(II) compounds, were very successful we implemented a systematic investigation of **2** as a reagent for the synthesis of sandwich and half-sandwich complexes with **1** as a ligand. The aim of the project is to determine both experimentally and theoretically the limits of simple concepts based on the analogy between phosphorus and carbon chemistry for the bonding characteristics of π ligands derived from unsaturated P-heterocycles. According to these principles, which include the diagonal relationship between the two elements[4] or the isolobal principle,[5] C−R fragments and phosphorus atoms should be freely exchangeable without significantly changing the properties of the substance in question.[4] We regard the analogy between phosphorus and carbon to be no longer valid if the formally analogous compounds differ significantly in their reactivity, spectroscopic properties, or geometric structure.

We now report the synthesis and the properties of manganese complexes with **1** as ligands. We are interested in this class of substances because we hope to obtain direct information about the singly occupied molecular orbitals (SOMOs) of the paramagnetic oligophosphamanganocenes, especially by EPR spectroscopy. The EPR parameters should provide us with information about the degree of similarity between the different manganocene derivatives.

If, for instance, triphenylstannyltriphosphole **2a** is treated with $[(CO)_5MnBr]$, triphosphacymantrene **3** is obtained in good yield.[6] As was also found for other triphospholyl complexes,[7] **3** can also be used as a σ ligand because of its phosphorus lone pairs. When it is treated with $[(CO)_5Cr(thf)]$, the binuclear Mn/Cr complex **4** forms, also in good yield. However, $MnCl_2$ proved to be unsuited for the synthesis of the hexaphosphamanganocene derivative **5**. The more soluble $[Mn\{N(SiMe_3)_2\}_2]$, however, can be treated with trimethylstannyltriphosphole **2b** to give **5**.







The triphosphacymantrene derivatives are diamagnetic and do not show any unexpected properties when compared with the prototype carbon compounds. The IR spectra of cymantrene and **3**, for example, each exhibit two ν(CO) peaks, that differ by at most 17 cm^{-1}. [8]

An X-ray crystal structure analysis[9] of **5** (Figure 1) showed, on first sight, that it is placed in a homologous series with other hexaphosphametallocenes.[10]

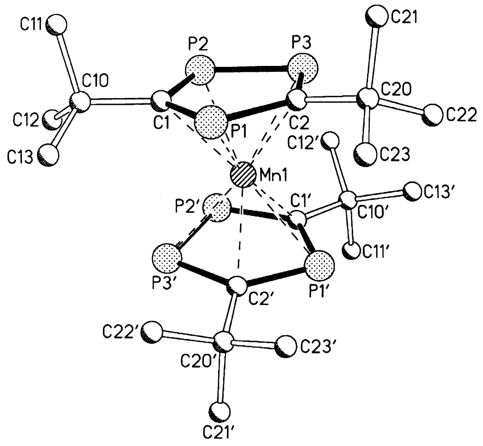


Figure 1. Molecular structure of **5** in the solid state. Hydrogen atoms are omitted for clarity.

Compound **5**, which is axially chiral because the ligands are twisted relative to each other, undergoes spontaneous separation of the enantiomers on crystallization. The angle between the planes of the two five-membered rings is 171.0(2)° and the distance between Mn and the ring centers (171 pm) lies between those of the analogous iron and chromium compounds.[10] Superconducting quantum interference device (SQUID) measurements showed **5** to be a low-spin compound.[11] The EPR spectra of **5** as liquid and frozen solutions (Figure 2) are far better resolved than those of manganocenes with purely carbacyclic ligands[12] and show the

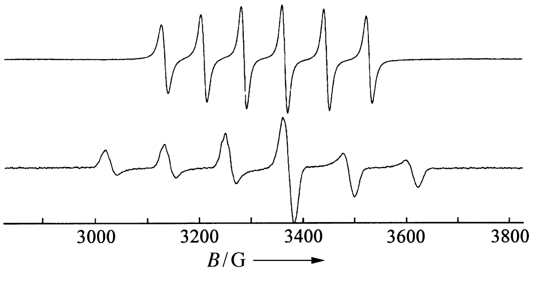


Figure 2. EPR spectra of **5** in *n*-hexane in the liquid phase at 293 K (above) and in the glassy, frozen solution at 100 K (below). For EPR parameters, see Experimental Section.

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characteristics of axially symmetric g- and a (^{55}Mn)-hyperfine tensors that are consistent with a ^{2}A ground state.[13] The lowering of the symmetry of the π ligand orbitals of **1**, caused by the P atoms, does not allow exactly degenerate frontier orbitals in **5** and thereby an exact axial symmetry for its SOMO is ruled out. However, the tensor components $g_\perp$ and $A_\perp$(^{55}Mn) could not be resolved and no hyperfine structure, due to the phosphorus or hydrogen nuclei, could be observed. This suggests a very small spin density on the ligands. The narrow linewidth of the spectra, the ^{55}Mn hyperfine structure, and the small g anisotropy indicate a nondegenerate spin state, spin density essentially centered on the metal, and a small spin–orbit coupling.[12] Compound **5** therefore has very different properties from the high-spin manganocene and also from the low-spin decamethylmanganocene, for which a Jahn–Teller active, degenerate $^2E_{2g}$ ground state was found and which is incompatible with the EPR properties of **5**.[12]

In order to characterize the electronic structure of **5** more completely, we calculated the structure and spin-density distribution with density functional theory. The calculations used Becke's three-parameter hybrid functional[14] combined with the Lee, Yang, and Parr's nonlocal correlation functional (B3LYP),[15] as implemented in Gaussian 98.[16] The Schäfer-Horn-Ahlrichs split-valence basis set[17] (SHAsv) was used for geometry optimizations and the subsequent frequency calculations. Additionally, we performed single-point calculations on the optimized geometries using the Schäfer-Horn-Ahlrichs triple-zeta basis set[17] (SHAtz) in order to obtain a more exact description of the electronic structure of **5**. Both basis sets were extended with a set of d functions with exponents of 0.6 and 0.34 on C and P, respectively, and of p and f functions with exponents of 0.092 and 0.96 on Mn.[18]

Starting from the crystal structure of **5**, two C_2-symmetrical minima were obtained for two different electronic states. One was the ^{2}A state expected on the basis of the EPR spectra and the other a ^{2}B state only 0.6 kcal mol^{-1} less stable. The energetic ordering of the two states can therefore not be determined clearly. Both wavefunctions proved to be stable.

Table 1 shows some selected bond lengths and angles for **5**. For the calculated ^{2}A state, the distance from the ring center to the metal (174 pm) and the torsional angle between the rings (81°) are in better accordance with the experimental values (171 pm, 76°) than for the ^{2}B (184 pm, 86°). When the calculated structures are superimposed on the crystal structure with the program VMD 1.2,[19] the ^{2}A structure thus gives a smaller root-mean-square distance[20] (RMSD) of 21 pm than the 34 pm RMSD of the ^{2}B structure. The calculated spin-density distributions for the two possible ground states of **5** are shown in Figure 3.[21] Both are clearly metal centered. The shape of the spin-density distribution of the ^{2}A state corresponds largely to a d_{z^2} orbital; in contrast, that for the ^{2}B state resembles a d_{xy} or $d_{x^2-y^2}$ orbital.

Table 1. Bond lengths in **5** [pm].

	exp.	^{2}A[a]	^{2}B[a]
Mn–P1	236.3(2)	240.6	252.1
Mn–P2	238.70(14)	242.8	244.1
Mn–P3	239.06(14)	243.0	246.8
Mn–C1	221.4(5)	222.9	230.1
Mn–C2	221.9(5)	227.4	239.3
P1–C1	176.9(5)	179.0	177.6
P1–C2	176.2(6)	178.6	177.0
P2–C1	177.9(5)	179.8	178.8
P3–C2	177.4(5)	179.2	178.5
P2–P3	213.1(2)	217.2	217.9

[a] B3LYP/SHAsv.

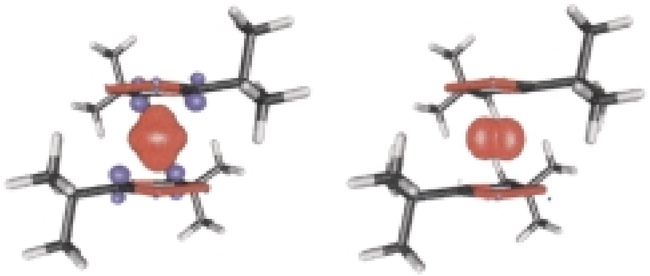

Figure 3. Calculated spin-density distribution of **5** for the ^{2}A (above) and ^{2}B (below) ground states. Isodensity contours are 0.006 e$^-$ b^{-3} (b = atomic unit bohr).

For **5**, the calculated isotropic and anisotropic ^{55}Mn hyperfine structures[22] are shown in Table 2. Taking the experimental error limits and the likely accuracy of the calculated results into account, there is reasonable agreement between the calculated and experimental values for the ^{2}A state. However, the deviation from axial symmetry found in the calculations is larger than the error limits of the experimental values allow. The ^{2}B state, on the other hand, is calculated to have a significantly smaller $\langle a(^{55}\mathrm{Mn})\rangle$ coupling constant and an inverted splitting pattern compared with experimental results. Such a splitting pattern is found for decamethylmanganocene, which has a $^2E_{2g}$ ground state that corresponds to the ^{2}B state for **5**[12, 23] (Figure 4).

Table 2. Isotropic and anisotropic hyperfine coupling constants of **5** [G].

	exp.	^{2}A[a]	^{2}B[a]
$\langle a(^{55}\mathrm{Mn})\rangle$	78.9 ± 3.6	−63.2	−44.8
A_{zz}	not resolved	6.0	−133.7
A_{xx}	115.7 ± 5.1	−92.9	−0.8
A_{yy}	115.7 ± 5.1	−102.7	0.1

[a] B3LYP/SHAtz//B3LYP/SHAsv.

There are two possible explanations of the reversal of the order of the frontier orbitals observed here. Cyclopentadienyl

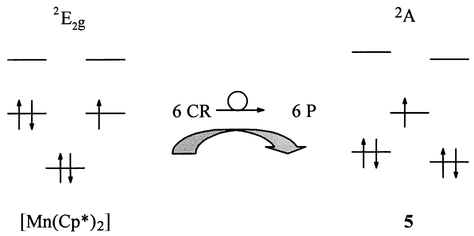

Figure 4. Schematic representation of the frontier orbitals of decamethylmanganocene and hexaphosphamanganocene **5**.

and triphospholyl ligands differ because of the lone pairs on phosphorus, which prodvide the possibility of interaction with the metal center. The calculations, however, showed no significant interaction with the d orbitals of the manganese center.[25] On the other hand, the size of the phosphorus atoms alone causes significant changes in the electronic properties of the ligands. Not only the spatial extent of the phosphorus p orbitals but also the ring diameter play a role. These two effects can change the interaction between the d orbitals of the metal and the orbitals of the ligand significantly and thereby change the nature of the frontier orbitals. Our data does not yet allow a clear assignment of these effects.

In summary, by introducing six phosphorus atoms into the manganocene framework in [bis(3,5-di(*tert*-butyl)-1,2,4-triphospholyl)manganese], **5** leads to a ^{2}A ground state, unprecedented for manganocene derivatives. Introducing three phosphorus atoms into each ligand thus results in a change in the energetic ordering of the frontier orbitals. The properties of hexaphosphamanganocene **5** can no longer be derived from simple P–C analogies. In contrast, triphosphacymantrene derivatives do not differ significantly from the prototype cymantrene. The π ligand 1,2,4-triphospholyl **1** thus represents a well suited system for determining the limits of the applicability of qualitative analogies between phosphorus- and carbon-based organic chemistry.

Experimental Section

3: A solution of 1-triphenylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphole **2a** (0.894 g, 2.26 mmol) in THF (6 mL) was treated at room temperature with $[Mn(CO)_5Br]$ (1.314 g, 3.25 mmol) in THF (10 mL). The mixture was refluxed for 2 h. After the volatile components were removed in vacuo, the red residue was distilled in a Kugelrohr apparatus. The fraction that distilled between 90 and 130 °C at 0.01 mbar was recrystallized from *n*-hexane to give of analytically pure **3** (0.50 g, 1.35 mmol, 61 %) in the form of yellow crystals; ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 1.24$ (s, 18 H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 222.2$ (s, CO), 161.9 (ddd, $^1J(^{31}P,^{13}C) = 79.2$ Hz, $^1J(^{31}P,^{13}C) + {}^2J(^{31}P,^{13}C) = 101$ Hz, C_{ring}), 39.7 (ddd, $^2J(^{31}P,^{13}C) = 17.4$ Hz, $^2J(^{31}P,^{13}C) + {}^3J(^{31}P,^{13}C) = 13.1$ Hz, $\mathit{C}(CH_3)_3$), 36.9 (ddd, $^3J(^{31}P,^{13}C) = 8.0$ Hz, $^3J(^{31}P,^{13}C) + {}^4J(^{31}P,^{13}C) = 8.3$ Hz, $C(\mathit{C}H_3)_3$); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): A_2B system, $\delta = 114.10$ (pd, $^2J(^{31}P,^{31}P) = 42.7$ Hz, 2 P, P(A)), 110.60 (pt, $^2J(^{31}P,^{31}P) = 42.7$ Hz, 1 P, P(B)); IR (THF): $\tilde{\nu} = 2019, 1952$ cm^{-1} (C=O); MS (FD): *m*/*z* (%): 370 (100) $[M]^+$; MS (EI, 70 eV): *m*/*z* (%): 370 (15) $[M]^+$, 314 (20) $[M - 2\,CO]^+$, 286 (100) $[M - 3\,CO]^+$; elemental analysis (%): calcd. for $C_{13}H_{18}MnO_3P_3$: C 42.18, H 4.90; found: C 42.50, H 4.86.

4: For the preparation of in situ $[Cr(CO)_5(thf)]$, $[Cr(CO)_6]$ (0.077 g, 0.35 mmol) was irradiated in THF (20 mL) for 3 h. A solution of **3** (0.114 g, 0.3 mmol) in THF (10 mL) was added at room temperature. The reaction mixture was stirred for 2 h at room temperature. The volatile components were removed in vacuo and the residue suspended in *n*-pentane and filtered. Crystallization from *n*-pentane yielded **4** (0.135 g, 0.24 mmol, 80 %) in the form of yellow-orange crystals; ^{1}H NMR (269.7 MHz, CD_2Cl_2, 25 °C): $\delta = 1.44$ (s, 9 H, $C(CH_3)_3$), 1.32 (s, 9 H, $C(CH_3)_3$); ^{31}P NMR (109.4 MHz, CD_2Cl_2, 25 °C): ABC system, $\delta = 77.6$ (dd, $^1J(^{31}P,^{31}P) = 438.5$ Hz, $^2J(^{31}P,^{31}P) = 36$ Hz, 1 P, P(A)), 100.4 (pt, $^2J(^{31}P,^{31}P) = 36$ Hz, $^2J(^{31}P,^{31}P) = 48.6$ Hz, 1 P, P(B)), 165.4 (dd, $^1J(^{31}P,^{31}P) = 438.5$ Hz, $^2J(^{31}P,^{31}P) = 48.6$ Hz, 1 P, P(C)); IR (THF): $\tilde{\nu} = 2072$ (s), 2023 (vs), 1998 (s), 1964 (vs, br), 1953 cm^{-1} (vs, br) (C=O); MS (FD): *m*/*z* (%): 562 (100) $[M]^+$.

5: $[Mn\{N(SiMe_3)_2\}_2]$, analogously with ref. [25], was prepared in situ from dry $MnCl_2$ (0.193 g, 1.53 mmol) and 5 mL of a 0.6 molar (3.07 mmol) toluene solution of $Na[N(SiMe_3)_2]$ in THF (20 mL). The solvents were removed in vacuo after completion of the reaction. A solution of 1-trimethylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphole **2b** (0.943 g, 2.39 mmol) in 25 mL of *n*-hexane was added to the manganese amide at −40 °C. The mixture was warmed to 20 °C. A red solution was formed and colorless $[(Me_3Si)_2NSnMe_3]$ precipitated. After stirring for 2 h and cooling slowly to −30 °C, **5** was obtained in the form of black crystals, which were washed several times at −50 °C with *n*-hexane, to give **5** (0.170 g, 0.328 mmol, 27.5 %). EPR (9.34 GHz, *n*-hexane, 298 K): $\langle g \rangle = 2.008 \pm 0.005$, $\langle a(^{55}Mn) \rangle = 78.9 \pm 3.6$ G (^{55}Mn (100 %): I = 5/2); EPR (9.42 GHz, *n*-hexane, 100 K): $g_{\parallel} = 2.00 \pm 0.02$, $A_{\parallel}(^{55}Mn) =$ unresolved, $g_{\perp} = 2.03 \pm 0.01$, $A_{\perp} = 115.7 \pm 5.1$ G (^{55}Mn (100 %): I = 5/2); the error limits given represent the maximum possible deviation from the mean value; MS (FD): *m*/*z* (%): 517 (100) $[M]^+$.

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Triple-Decker Type Coordination of a Fullerene Trianion in $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$—Single Crystal Structure and Magnetic Properties**

Thomas F. Fässler,* Rudolf Hoffmann,
Stefan Hoffmann und Michael Wörle

Dedicated to Professor Hans-Herbert Brintzinger
on the occasion of his 65th birthday

Molecular conductors are promising candidates for high-temperature superconductors because large phonon frequency bands with little dispersion and hence a large density of state at the Fermi level (E_F) are possible. The alkali metal – fullerides A_3C_{60} (A is the alkali metal) are a fascinating class of compounds showing superconductivity up to 40 K.[1, 2] The trianions of the C_{60} fullerenes play a deciding role in understanding the superconductivity, and, therefore, the nature of the electronic ground state of $[C_{60}]^{3-}$ and its intermolecular interactions are of particular interest. The LUMO of a C_{60} molecule with I_h-symmetry is threefold degenerate, has t_{1u}-symmetry, and can be occupied by up to six electrons. In A_3C_{60} compounds these orbitals form a small electronic band which is half filled with electrons and is responsible for the metallic conductivity (Figure 1). The occupation of the molecular LUMOs of C_{60} by a further three electrons is expected to result in energetically low-lying quartet (^{4}A) and doublet states (^{2}H and ^{2}T). The doublet states are Jahn – Teller-unstable systems and structural distortion is possible (Figure 1).[3–5] In spite of these interesting findings, there is still not a single crystal structure determination of a binary superconducting phase. Overlapping reflections, in refinements based upon X-ray and neutron powder diffraction studies, give plenty of scope for discussion as to the nature of the conformational disorder found in the K_3C_{60} fullerene molecules.[6–8]

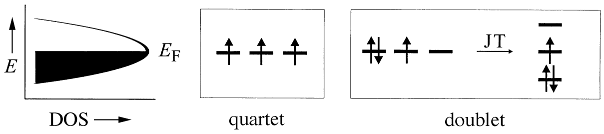

Figure 1. The three fold degenerate HOMO of the $[C_{60}]^{3-}$ ions with I_h symmetry (center) and the resulting density state (DOS) of the corresponding half-filled band in K_3C_{60} (left). In the doublet states, Jahn – Teller (JT) distortion is possible (right).

In the course of our investigations of soluble Zintl ions of the carbon group,[9, 10] we recently reported the reduction of C_{60} with potassium in DMF and the crystallization of a fullerene dianion with cryptands. In $[K([2.2.2]crypt)]_2[C_{60}](C_6H_5CH_3)_4$ (**2**),[11] following the principle of spherical close packing, the $[C_{60}]^{2-}$ units form layers which are separated from each other by bulky $[K^+([2.2.2]crypt)]$ ions (Figure 2a and b).[12] In attempting to prepare homoatomic anions of the heavier homologues of the carbon group by a one-pot synthesis, we chose to try the reduction of the elements tin and lead with alkali earth metals in the molten crown ether [18]crown-6.[13–16] Using fullerenes in this synthetic procedure has now enabled us to perform a single crystal structure determination of a salt containing two ordered C_{60} trianions. We now report the synthesis, and structural and magnetic properties of the complex $[K([18]crown\text{-}6)]_3[C_{60}](C_6H_5CH_3)_2$ (**1**).

Potassium dissolves in the molten crown ether [18]crown-6 at 313 K to give a deep blue solution. Carbon is added to the melt in the form of C_{60}. After the blue coloration disappears, DMF is added to the reaction mixture. Crystals of the title compound are then obtained by layering extracts of the reaction mixture with toluene [Eq. (1)]. The crystals are black cuboids which when crushed have a red hue.

$$C_{60} \xrightarrow[\text{DMF, toluene}]{\text{[18]crown-6, K}} [K([18]crown\text{-}6)]_3[C_{60}](C_6H_5CH_3)_2 \quad \mathbf{1} \qquad (1)$$

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