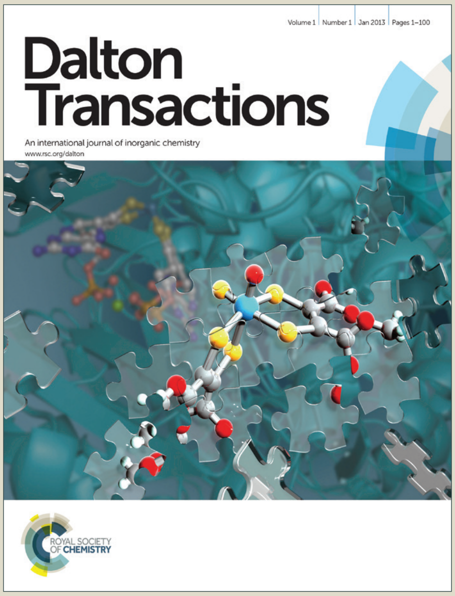
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis and Characterization of Manganese Triple-Decker Complexes

Sebastian Heinl, Gabor Balázs, Michael Bodensteiner and Manfred Scheer*[a]

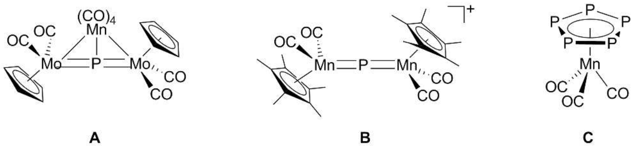
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The use of the highly sterically demanding Cp^{BIG} ligand (Cp^{BIG} = C_5(4-*n*BuC_6H_4)$_5$) and white phosphorus (P_4) enables the synthesis of new P-rich derivatives of the rare P_n ligand complexes of manganese. The obtained complexes, [{Cp^{BIG}Mn}$_2$(μ,η$^{5:5}$-P_5)] (**2**) and [{Cp^{BIG}Mn}$_2$(μ,η$^{2:2}$-P_2)$_2$] (**3**), exhibit the highest number of P atoms within this class of manganese compounds identified by X-ray structure analyses. The EPR spectrum of the 29 VE triple-decker complex **2** shows one unpaired electron coupling with two 5/2 spin Mn nuclei.

Introduction

Since Ginsberg and Lindsell[1] first reported on the synthesis of complexes with substituent-free phosphorus ligands, numerous so-called P_n ligand complexes were prepared and described in literature.[2] In most cases, the tetrahedral molecule P_4 is the starting material of choice.[3] Up to now, P_n ligand complexes are known for almost all transition metals[4] and a large number of main group elements.[5] However, there are some unexplored spots within the d-block elements, where no or only very few compounds with substituent-free P_n ligands are known. The 7th group might be seen as a border between the early and the late transition metals, where in both latter cases a certain number of substances with P_n units are known. The absence of technetium derivatives can most likely be explained by its artificial and radioactive nature. However, while for rhenium several compounds are known, for manganese only very few examples exist.[4] To the best of our knowledge, the only crystallographically characterized P_n ligand complex of manganese is [{CpMo(CO)$_2$}$_2${Mn(CO)$_4$}(μ$_3$-P)}] (**A**) with a P_1 unit, reported by Mays et al. (Scheme 1).[6] Huttner et al. also reported on Mn containing dimetallaphosphacumulenes **B** containing P_1 units.[7] The only Mn complex with a P_n moiety with n > 1 was described by Baudler et al. in 1991 as [(CO)$_3$Mn(η^5-P_5)] (**C**). [8] Due to the limited characterization of **C** its existence is questionable (cf. SI). There are also several other examples of P_n ligand complexes with direct Mn–P bonds. However, they are based on the coordination of the phosphorus lone pair towards 16 valence electron (VE) {CpMn(CO)$_2$} fragments.[4]

The lack of manganese complexes with substituent-free P_n ligands prompted us to investigate this class of compounds. Herein, we report on the synthesis of the precursor complex [Cp^{BIG}Mn(cht)] (**1**; Cp^{BIG} = C_5(4-*n*BuC_6H_4)$_5$; cht = cycloheptatriene) and its reaction with P_4 forming the first triple-decker complexes of manganese [{Cp^{BIG}Mn}$_2$(μ,η$^{5:5}$-P_5)] (**2**) and [{Cp^{BIG}Mn}$_2$(μ,η$^{2:2}$-P_2)$_2$] (**3**). The compounds were characterized by NMR and EPR spectroscopy, mass spectrometry, single crystal X-ray diffraction as well as by DFT calculations.



Scheme 1. Reported P_n ligand complexes of manganese.

Results and discussion

The UV irradiation of the sterically crowded cymantrene derivative [Cp^{BIG}Mn(CO)$_3$][9] in toluene with an excess of cycloheptatriene (cht) results in the substitution of all three carbonyl groups by one cht ligand (Equation 1). After filtration over Celite, [Cp^{BIG}Mn(cht)] (**1**) is obtained pure as a brown powder in 90% yield. Interestingly, if silica gel is used instead of Celite, decomposition is observed. As expected, complex **1** exhibits a sandwich structure with a η^6 bound cht ligand and the methylene group pointing away from the {Cp^{BIG}Mn} fragment (Figure 1). This methylene group is disordered over two positions (occupancies of 78% and 22%). The structural parameters compare rather well with the only other structurally known cht-Mn complex [(C_5H_4Me)Mn(cht')] (cht' = 1-phenylcycloheptatriene).[10] In both cases no alternating bond lengths in the triene moiety is observed, which were also found for other η^6-cht complexes.[11] In **1** this can be explained by the disorder discussed above.

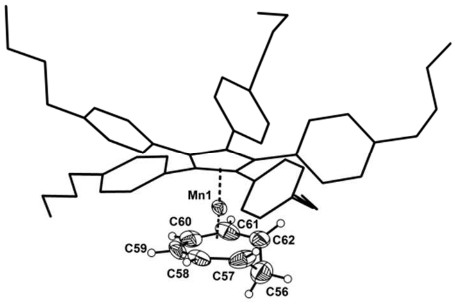
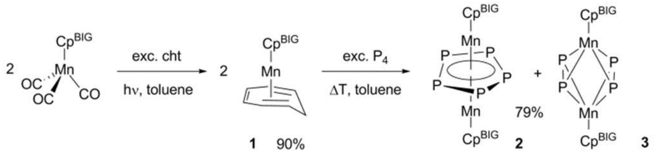


Figure 1. Molecular structure of **1** in the crystal. Thermal ellipsoids are drawn at 50% probability level. Because of disorder, only the main part is depicted. H atoms on the Cp^{BIG} ligand are omitted for clarity and it is drawn in 'wire-or-stick' model. Selected bond lengths [Å] and angles [°]: Mn1···C56/C56' 2.749(3)/2.789(11), Mn1-C57/C57' 2.173(3)/2.220(12), Mn1-C58 2.109(2), Mn1-C59 2.110(2), Mn1-C60 2.114(2), Mn1-C61 2.084(2), Mn1-C62 2.143(2), C56/C56'-cht_{Plane} 115.7(3)/113.8(8).

The precursor complex **1** reacts with P_4 in toluene in a co-thermolysis reaction under elimination of the cht ligand. Chromatographic workup affords one single brown fraction of a mixture of $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (**2**) and $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**3**), which could not be separated from each other even by thin-layer chromatography (Equation 1). Single crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution as solvate with six toluene molecules per formula unit. Both compounds co-crystallize on the same crystallographic position. Therefore, effectively a triple-decker complex with a disordered middle-deck is observed. Accordingly to the occupancies of the *cyclo*-P_5 ligand (70%) and that of the two P_2 ligands (30%), a 7:3 mixture of **2** and **3** is obtained (Figure 2). The P1 and P2 atoms belong to both complexes. This composition is also confirmed by the elemental analysis. The P–P bond lengths in **2** are with an average value of 2.20 Å in good agreement with other known triple-decker complexes containing a *cyclo*-P_5 middle-deck (2.15 Å - 2.28 Å).[12]



Binuclear compounds with two bridging P_2 units are rare, only $[(Cp^RCo)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (Cp^R = Cp''',[13] Cp*)[14] and $[(Cp^*Fe)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$[14] are known. In complex **3** the bond lengths P1–P2 and P6–P7 are in between a single and a double bond with 2.150(2) Å and 2.123(8) Å and roughly 0.1 Å longer than in the previously described cobalt and iron examples. The Cp^{BIG} ligands in **2** and **3** are not co-planar but tilted against each other by 8.80(11)° and by 4.40(6)° against the phosphorus middle-decks. In complex **2**, the Cp^{BIG} moieties and the P_5 ring are almost eclipsed (~10°), which results in a staggered conformation of the P_5 ring and the downward orientated Ph groups. This is also the case for the pentaphosphaferrocene $[Cp^{BIG}Fe(\eta^5\text{-}P_5)]$.[15] An further interesting feature of **2** and **3** is the Mn1–Mn1' distance of 2.7953(9) Å, which is in an usual range for Mn–Mn single bonds (CCDC search: 2.5 – 3.1 Å).

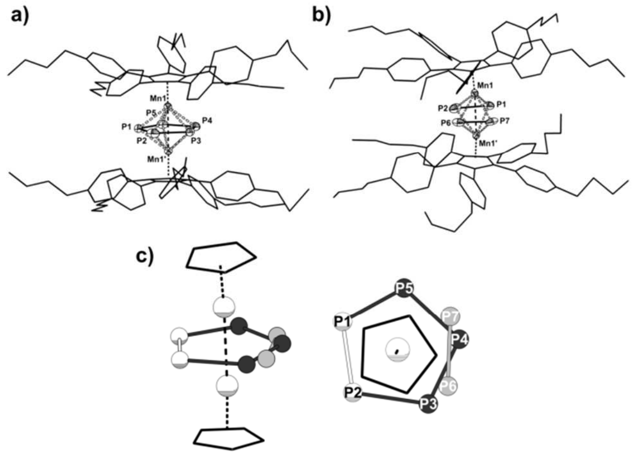


Figure 2. Molecular structures of a) **2** and b) **3** in the crystal. For clarity C atoms are shown in 'wire-or-stick' model and H atoms and solvent molecules are omitted. Ellipsoids are drawn at 50% probability level. c) Schematic illustration of the disorder of **2** and **3** in the crystal (left: side view; right: top view). Different parts are colored differently; hashed globes belong to both parts. Selected bond lengths [Å] and angles [°] of **2**: Mn1-Mn1' 2.7953(9), P1-P2 2.150(2), P2-P3 2.291(2), P3-P4 2.157(2), P4-P5 2.262(2), P1-P5 2.114(2), Mn1-P1 2.3295(7), Mn1-P2 2.3276(8), Mn1-P3 2.3283(10), Mn1-P4 2.3407(12), Mn1-P5 2.3369, Angle between P_5 and Cp 4.40(6), angle between Cp^{BIG} ligands 8.80(11). Selected bond lengths [Å] and angles [°] of **3**: Mn1-Mn1' 2.7953(9), P1-P2 2.150(2), P6-P7 2.123(8), P1···P7 3.243(4), P2···P6 2.843(4), Mn1-P1 2.3295(7), Mn1-P2 2.3276(8), Mn1-P6 2.319(2), Mn1-P7 2.342(3), angle between $(P_2)_2$ and Cp 4.40(6), angle between Cp^{BIG} ligands 8.80(11), angle between P_2 units 10.75(15).

In the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 of dissolved crystals, which represent a mixture of **2** and **3**, only one broadened singlet is observed at δ = 396.9 ppm ($\omega_{1/2}$ = 467 Hz). Therefore, the signal of one of the two compounds is not observed, or **2** and **3** have incidentally the same chemical shifts. Since **2** is calculated to have a triplet spin state, it is very likely that the observed signal corresponds only to **3**. By cooling a solution in CD_2Cl_2, in the NMR spectrum the signal steadily sharpens, which is accompanied by an intensity decrease. At 213 K the signal is not observed anymore. Heating-up a solution in toluene-d_8 to temperatures up to 373 K results in a further broadening of the signal. The ^1H NMR spectrum shows several superimposed signals, which cannot further be assigned to a particular Cp^{BIG} ligand of the products. Cooling the sample to 193 K does not result in the splitting of the signal (see supporting information for spectra). The NMR behavior might be explained by the odd number of valence electrons in complex **2**, making the sample paramagnetic.

EPR measurements at room temperature in toluene do not show an EPR signal, as would be expected for the 29 VE triple-decker complex **2**. However, the spectrum at 77 K shows a well resolved anisotropic multiplet (Figure 3). The splitting can be explained by coupling of the electron with two Mn centers with a spin of 5/2 each. The g_{iso} value was identified to 1.9228 G (simulation). This is slightly smaller than the value of 1.9571 G we obtained by DFT calculations.[16] The absence of an EPR signal at room temperature can be explained with a rapid relaxation process.

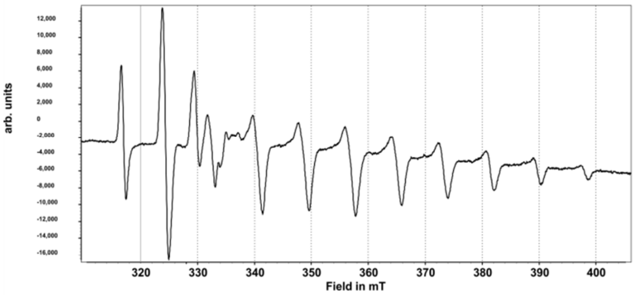


Figure 3. EPR spectrum of a mixture of **2** and **3** in toluene at 77 K.

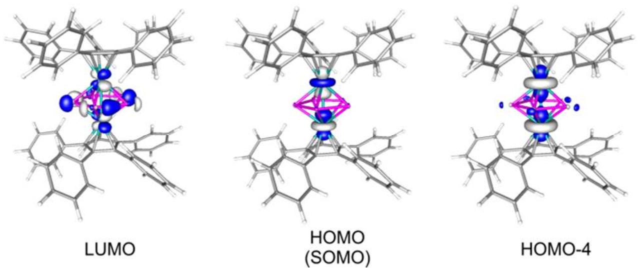


Figure 4. Selected α-spin molecular orbitals of $[\{(C_5Ph_5)Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (**2'**), calculated at the BP86/def2-SVP level of theory.

The LIFDI mass spectrum of a solution of the crystals exhibits the base peak at m/z = 1716.4 corresponding to **2**. The peak for **3** (m/z = 1685.6) can be detected with a relative intensity ca. 25%, which is in good agreement with the product distribution obtained from the X-ray analysis.

To gain more insight into the electronic structure of **2**, DFT calculations have been performed on the model compound $[\{(C_5Ph_5)Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (**2'**).[16] For comparison to other triple-decker complexes with inorganic middle-decks see ref. [17]. The geometric parameters of the optimized structure of **2'** in the doublet spin state are in agreement with the experimental values determined by X-ray diffractions. The calculated Mn–Mn distance in **2'** is 2.878 Å, which is slightly longer than the experimentally determined value of 2.7953(9) Å for **2**. Interestingly, the optimized geometry of **2'** in the excited, quartet spin state differs considerably from the experimental geometry, and is 67.31 kJ mol^{-1} higher in energy. In the quartet spin state the P_5 middle deck adopts an envelope conformation with a $\mu,\eta^{4:3}$ coordination mode. The Mn–Mn distance is 3.164 Å, considerably longer than the corresponding distance in the doublet spin state. All these results suggest that the ground spin state of **2'** is a doublet, which could be definitely proven by the simulation of the EPR spectrum. According to the calculations, the unpaired electron is equally localized on both manganese atoms. The single occupied molecular orbital (SOMO) is the highest occupied molecular orbital (Figure 4). It represents an out-of-phase combination of the d_{z^2} orbitals of the two manganese atoms. Since the in-phase combination is doubly occupied, a Mn–Mn bond order of 0.5 results. This is also confirmed by the calculated Wiberg bond index of 0.6. The localized molecular orbital representing the Mn–Mn bond is depicted in Figure 5.

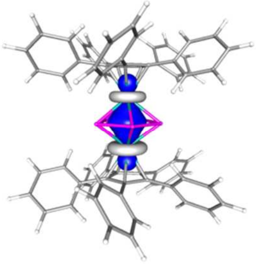


Figure 5. Localized molecular orbital representing the Mn–Mn bond in $[\{(C_5Ph_5)Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (**2'**). Calculated at the BP86/def2-SVP level of theory.

The geometry of the model compound $[\{(C_5Ph_5)Mn\}_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**3'**) has been optimizes using the same functional and basis set as for **2'**. The ground state of **3'** could be calculated to be a singlet. This explains the absence of a signal of **3** in the EPR spectrum. The optimized geometry shows a short Mn–Mn distance of 2.597 Å which is shorter than the corresponding distance in **2'** (Mn–Mn 2.878 Å) as well as the experimentally determined distance (2.7953(9) Å). This is probably a result of the overestimation of the Mn–Mn interaction in **3'**. The presence of a Mn-Mn bond is clearly indicated by the Localized Molecular Orbitals (Figure 6). Furthermore, the Wiberg Bond Index for the Mn-Mn bond is high (1.18) and indicates a very strong bond. Similarly high bond orders were obtained for the Mn–P (0.97) and P–P (0.84 and 0.86) bonds. The Natural Population Analysis shows a moderate charge separation. The two Mn atoms carry a partial positive charge of 0.45 each, while the negative partial charge is delocalized over the Cp ligands.

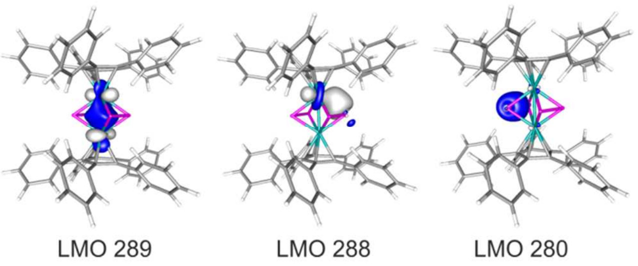


Figure 6. Selected localized molecular orbitals representing the Mn–Mn, Mn–P and P–P bond in $[\{(C_5Ph_5)Mn\}_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**3'**). Calculated at the BP86/def2-SVP level of theory.

In summary, we reported on the synthesis of two novel triple-decker complexes $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (**2**) and $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**3**), the so far P-richest manganese compounds characterized by X-ray crystallography. They represent two new derivatives of the rare class of P_n ligand complexes of manganese. The compounds were characterized by single crystal X-ray diffraction, mass spectrometry, VT NMR and EPR spectroscopy and elemental analysis. DFT calculations confirmed a doublet ground state for **2** with a Mn–Mn bond through the *cyclo*-P_5 ligand with calculated Wiberg bond index of 0.6.

Acknowledgments

This work was supported be the Deutsche Forschungsgemeinschaft. S. Heinl is grateful to the Fonds der Chemischen Industrie for a PhD fellowship. Prof. Dr. Hans-Jörg Himmel and Hendrik Herrmann (University of Heidelberg, Germany) are gratefully thanked for recording the LIFDI mass spectrum of **2**/**3**.

Experimental details

General remarks

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and Schlenk techniques. The solvents toluene, hexane and C_6D_6 were refluxed over potassium and distilled and degassed prior to use. The same procedure was applied for CD_2Cl_2 by using CaH_2 as drying reagent. Cht was used as obtained from *abcr GmbH* and $[Cp^{BIG}Mn(CO)_3]$ was prepared according to literature procedure.[9] The NMR spectra were measured on a Bruker Avance 300, 400, or 600 spectrometer. LIFDI-MS spectra were measured on a Finnigan MAT 95 (**1**) or a JOEL JMS-700 (**2**, **3**) mass spectrometer. The elemental analyses were determined on a Vario EL III apparatus. The IR spectra were measured on a VARIAN FTS-800 FT-IR spectrometer. For irradiations a TQ150-Z1 Hg lamp from Heraeus was used. The X-band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.5 GHz and rectangular resonator TE102 of the company Magnettech GmbH.

Synthesis of $[Cp^{BIG}Mn(cht)]$ (1):

A solution of $[Cp^{BIG}Mn(CO)_3]$ (1.0 g, 1.16 mmol) in 50 mL toluene is irradiated together with cht (0.32g, 0.36 mL, 3.46 mmol) for 30 min. The brown reaction mixture is filtered through Celite and carefully dried in vacuum. Compound **1** is obtained as a brown powder (914 mg, 90%).

1: $[C_{62}H_{73}Mn]$ calc.: C, 85.28; H, 8.43. found: C, 84.90; H, 8.37. LIFDI-MS (toluene): *m/z* (%) = 872.7 (100%, $[M]^+$), 818.9 (30%, $[Cp^{BIG}H+cht]^+$, Diels-Alder product). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1917 (s), 1858 (s). ^1H NMR (C_6D_6): δ [ppm] = 0.10 (d, $^3J_{HH}$ = 12.1 Hz, 1H, CH_2-cht), 0.82 (t, $^3J_{HH}$ = 6.8 Hz, 30H, ^nBu), 1.22 (m, 20H, ^nBu), 1.47 (m, 20H, ^nBu), 2.42 (t, $^3J_{HH}$ = 7.3 Hz, 20H, ^nBu), 2.79 (q, $^3J_{HH}$ = 10.0 Hz, 1H, CH_2-cht), 3.06 (s, 2H, CH-cht), 5.03 (s, 2H, CH-cht), 5.97 (s, 2H, CH-cht), 6.88 (d, $^3J_{HH}$ = 7.0 Hz, 20H, Ph), 7.24 (d, $^3J_{HH}$ = 7.0 Hz, 20H, Ph); see also supplementary information. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ [ppm] = 14.1 (*n*Bu), 22.2 (CH_2-cht), 22.7 (*n*Bu), 33.5 (*n*Bu), 35.6 (*n*Bu), 91.0 (CH-cht), 91.4 (CH-cht), 92.5 (CH-cht), 132.7 (Ph), 134.1 (Ph), 140.7 (Ph); one Ph signal is obscured by the C_6D_6 signal.

Synthesis of $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{5:5}\text{-}P_5)]$ (2) and $[\{Cp^{BIG}Mn\}_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (3):

A solution of $[Cp^{BIG}Mn(cht)]$ (400 mg, 0.46 mmol) and P_4 (284 mg, 2.3 mmol) in 100 mL toluene is refluxed for 16 h. The brown reaction mixture is dried in vacuum. Column chromatographic work-up (25 x 3 cm, hexane/toluene 2:1, silica) of the residue affords one brown fraction of a mixture of **2** and **3**. A co-crystallized product mixture is obtained from a concentrated toluene solution (310 mg, yield 79%).

Mixture of **2** and **3**: [70% **2** / 30% **3**] calc.: C, 77.37; H, 7.67. found: C, 77.76; H, 7.64. LIFDI-MS (toluene): *m/z* (%) = 1716.4 (100%, $[\mathbf{2}]^+$), 1686.6 (25%, $[\mathbf{3}]^+$), 726.3 (60%, $[Cp^{BIG}]^+$). ^1H NMR (C_6D_6): δ [ppm] = 0.73 (s-br, 30H, ^nBu), 1.09 (s-br, 20H, ^nBu), 1.29 (s-br, 10H, ^nBu), 1.41 (s, 10H, ^nBu), 2.18 (s-br, 10H, ^nBu), 6.2 (very broad, $\omega_{1/2}$ = 236 Hz, 5H), 6.67 (s-br, 10H, Ph), 7.31 (s-br, 10H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ [ppm] = 396.9 (s-br, $\omega_{1/2}$ = 467 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ [ppm] = 14.1 (CH_3), 22.8 (CH_2), 33.4 (CH_2), 35.8 (CH_2), 118.5 (Cp), 127.9 (Ph), 131.3 (Ph), 140.5 (Ph), 141.6 (Ph).

Notes and references

[a] *University of Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany. Fax: +49 941 943 4439; Tel: +49 941 943 4440; E-mail: manfred.scheer@chemie.uni-regensburg.de*

† Details of the X-ray structure analysis can be found in the supplementary information. CCDC-1048598-10468599. Electronic Supplementary Information (ESI) available: Full crystallographic data, NMR spectra. See DOI: 10.1039/b000000x/

‡ The presented results are part of the doctoral thesis of Sebastian Heinl. Heinl, S. PhD thesis, University of Regensburg (Regensburg, Germany), **2014**.

[1] A. P. Ginsberg, W. E. Lindsell, *J. Amer. Chem. Soc.* 1971, **93**, 2082-2084.

[2] a) O. J. Scherer, *Angew. Chem.* 1990, **102**, 1137-1155. b) V. M. Di, P. Stoppioni, M. Peruzzini, *Polyhedron* 1987, **6**, 351-382.

[3] B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* 2010, **110**, 4164-4177.

[4] a) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* 2010, **110**, 4178-4235; for a recent example cf.: b) S. Heinl, E. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 10887 – 10891.

[5] a) M. Scheer, G. Balazs, A. Seitz, *Chem. Rev.* 2010, **110**, 4236-4256. b) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* 2011, **255**, 1342-1359.

[6] A. J. Bridgeman, M. J. Mays, A. D. Woods, *Organometallics* 2001, **20**, 2932-2935.

[7] A. Strube, J. Heuser, G. Huttner, H. Lang, *J. Organomet. Chem.* 1988, **356**, C9-C11.

[8] M. Baudler, T. Etzbach, *Angew. Chem., Int. Ed.* 1991, **30**, 580-582.

[9] S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem., Int. Ed.* 2013, **52**, 10887-10891.

[10] J. A. D. Jeffreys, J. MacFie, *J. Chem. Soc., Dalton Trans.* 1978, 144-147.

[11] a) M. L. H. Green, N. M. Walker, *J. Chem. Soc., Chem. Commun.* 1989, 850-852. b) C. Jiabi, Y. Jienguo, L. Guixin, X. Weihua, S. Meicheng, Z. Zeying, T. Youqi, *J. Organomet. Chem.* 1980, **329**, 69-83. c) B. Klingert, G. Rihs, *J. Chem. Soc., Dalton Trans.* 1991, 2749-2760. d) T. Meyer-Friedrichsen, H. Wong, Marc H. Prosenc, J. Heck, *Eur. J. Inorg. Chem.* 2003, **2003**, 936-946.

[12] a) O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim, R. Gross, *Angew. Chem., Int. Ed.* 1986, **25**, 363-364. b) Alexander R. Kudinov, Dmitry A. Loginov, Zoya A. Starikova, Pavel V. Petrovskii, M. Corsini, P. Zanello, *Eur. J. Inorg. Chem.* 2002, **2002**, 3018-3027. c) O. J. Scherer, T.

Brück, G. Wolmershäuser, *Chem. Ber.* 1989, **122**, 2049-2054. d) L. Y. Goh, R. C. S. Wong, C. K. Chu, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* 1990, 977-982.

[13] a) O. J. Scherer, G. Berg, G. Wolmershäuser, *Chem. Ber.* 1995, **128**, 635-639. b) F. Dielmann, M. Sierka, A. V. Virovets, M. Scheer, *Angew. Chem., Int. Ed.* **2010**, *49*, 6860-6864.

[14] M. E. Barr, L. F. Dahl, *Organometallics* 1991, **10**, 3991-3996.

[15] S. Heinl, G. Balázs, M. Scheer, *Phosphorus, Sulfur Silicon Relat. Elem.* 2014, **189**, 924-932.

[16] For details on DFT calculations and EPR simulation see supporting information.

[17] W. Tremel, R. Hoffmann, M. Kertesz, *J. Am. Chem. Soc.* **1989**, *111*, 2030-2039.

Graphical abstract

The synthesis and characterization (experimental and DFT) of sterically encumbered triple-decker complexes of the very rare class of P_n ligand complexes of manganese is reported.