Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
ARTICLE

DOI: 10.1002/zaac.201600047

Synthesis and Characterization of Manganese(I) Carbonyl Complexes of the Type $[(OC)_4Mn\{\mu\text{-}P(R)Aryl\}]_2$

Ralf Mede,[a] Sascha Blohm,[a] Helmar Görls,[a] and Matthias Westerhausen*[a]

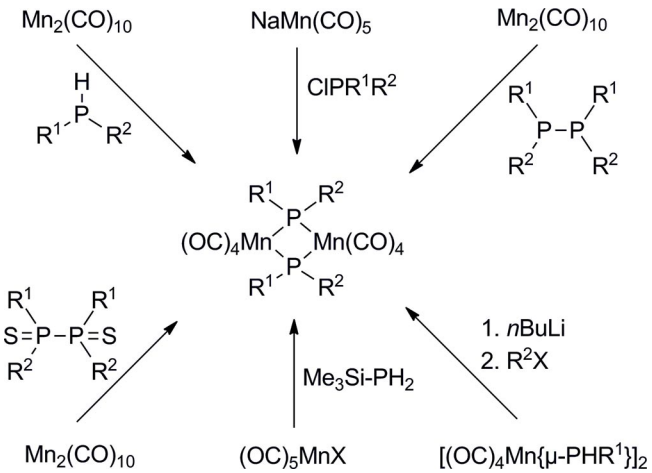
Keywords: Manganese; Carbonyl complexes; Metal carbonyls; Phosphanes; Phosphanides

Abstract. Metalation of secondary phosphanes HP*RR′* [*R* = *R′* = C_6H_4-4-Me, C_6H_3-3,5-Me_2 (**3**), C_6H_4-4-NMe_2 (**4**); *R*/*R′* = Ph/*c*Hex] with $Mn_2(CO)_{10}$ in boiling xylene (mixture of isomers), until the evolution of gaseous carbon monoxide ceases, leads to the formation of the dinuclear complexes of the type $[(OC)_4Mn(\mu\text{-}PRR')]_2$ [*R* = *R′* = C_6H_4-4-Me (**5**), C_6H_3-3,5-Me_2 (**6**), *R*/*R′* = Ph/*c*Hex (**7**), *R* = *R′* = C_6H_4-4-NMe_2 (**8**)] with poor to moderate yields. These manganese(I) complexes are only sparingly soluble or even nearly insoluble in hydrocarbons at room temperature. Planar four-membered Mn_2P_2 rings represent the central moiety with four carbonyl ligands at each manganese(I) atom. The steric demand of the P-bound substituents influences the Mn–P bond lengths as well as the P–Mn–P bond angles.

Introduction

Very recently the suitability of manganese(I) thiolates as CO releasing molecules (CORMs) to administer the signaling molecule carbon monoxide for biochemical, biological, and medicinal applications was studied.[1] The preferred synthetic route to these thiolate complexes involves the metalation of thiols with $Mn_2(CO)_{10}$, commonly yielding mixtures of dinuclear and tetranuclear complexes of the types $[(OC)_4Mn(\mu\text{-}SR)]_2$ and $[(OC)_3Mn(\mu_3\text{-}SR)]_4$ with bridging thiolato ligands. Alternatively, the metathetical approach via the reaction of $[(OC)_5MnBr]$ with K*SR* also proofed to offer a suitable access to these complexes. In contrast to the common di- and tetranuclear molecular structures, the 2,4,6-trimethylphenyltiolato manganese(I) complex precipitated as the trinuclear complex $[(OC)_4Mn(\mu\text{-}SMes)]_3$ (Mes = C_6H_2-2,4,6-Me_3, mesityl) with a six-membered Mn_3S_3 ring.[1] In complexes with carbonyl ligands trans-arranged to each other, a weakening of the Mn–CO bond has been observed by IR spectroscopy and X-ray structure determination. Consequently, the tetranuclear heterocubane-type complexes form due to the fact that a free electron pair at sulfur competes with such a carbonyl ligand; liberation of CO and related ligand exchange then converts dinuclear $[(OC)_4Mn(\mu\text{-}SR)]_2$ into tetranuclear $[(OC)_3Mn(\mu_3\text{-}SR)]_4$. The ease of exchange of one carbonyl ligand by Lewis bases has also been shown by dissolution of $[(OC)_4Mn(\mu\text{-}SR)]_2$ in dimethylsulfoxide (dmso) yielding $[(OC)_3(dmso)Mn(\mu\text{-}SR)]_2$. In order to suppress this ligand exchange and to stabilize manganese(I) complexes with carbonyl ligands in *trans* positions to each other, an anionic ligand without a second free electron pair was chosen and the isolobal phosphanides of the type $[(OC)_4Mn\{\mu\text{-}P(R)Aryl\}]_2$ was studied.

The manganese(I) carbonyl phosphanides represent a substance class with a long history of more than 50 years. Several strategies have been developed for the preparation of dinuclear $[(OC)_4Mn\{\mu\text{-}PRR'\}]_2$ (Scheme 1) (*R* = H, F, aryl, alkyl):



Scheme 1. Preparative protocols for the synthesis of dinuclear manganese(I) complexes of the type $[(OC)_4Mn\{\mu\text{-}PR^1R^2\}]_2$ (for assignment of R^1 and R^2 see text).

(i) First preparative protocols describe the metathetical approach of $NaMn(CO)_5$ with $ClPR_2$ (*R* = Ph,[2,3] Me);[3] especially the phenyl derivative $[(OC)_4Mn\{\mu\text{-}PPh_2\}]_2$ was accessible only with poor yields.

(ii) The oxidative addition of tetraphenyldiphosphane to manganese carbonyl gave $[(OC)_4Mn\{\mu\text{-}PPh_2\}]_2$ with yields up to 46 %.[3]

* Prof. Dr. M. Westerhausen
Fax: +49 3641 948132
E-Mail: m.we@uni-jena.de
Homepage: http://www.lsac1.uni-jena.de/
[a] Institute of Inorganic and Analytical Chemistry
Friedrich Schiller University Jena
Humboldtstraße 8
07743 Jena, Germany

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201600047** or from the author.

(iii) The reaction of $(OC)_5MnX$ (X = Cl, Br) with trimethylsilylphosphane ($R^1 = R^2 = H$)[4] and trimethylsilyldiphenylphosphane ($R^1 = R^2 = Ph$)[5] yielded a mixture of dinuclear and trinuclear cyclic $[(OC)_4Mn\{\mu\text{-}PH_2\}]_n$ (n = 2, 3) and volatile Me_3SiX. Coupling constants were elucidated from higher order NMR spectra for $[(OC)_4Mn\{\mu\text{-}PH_2\}]_n$, verifying the di- ($n$ = 2) and trinuclear (n = 3) nature of these complexes. However, the use of the manganese carbonyl iodide yielded $[\{(OC)_4Mn\}_2\{\mu\text{-}PH_2\}(\mu\text{-}I)]$ under similar reaction conditions.[4]

(iv) The addition of phosphanes to manganese carbonyl also allowed the isolation of $[(OC)_4Mn\{\mu\text{-}PRR'\}]_2$ (R, R' = H, Ph, Me, *c*Hex) with rather poor yields.[6–9] The reaction of $Mn_2(CO)_{10}$ with H_2P-*c*Hex gave desired $[(OC)_4Mn\{\mu\text{-}P(H)cHex\}]_2$ with a yield of 10.5 % and the side-product $[\{(OC)_4Mn\}_2\{\mu\text{-}P(H)cHex\}(\mu\text{-}H)]$ with a yield of 40.8 %.[8]

(v) The reduction of $R_2P(S)\text{-}P(S)R_2$ with $Mn_2(CO)_{10}$ yielded a mixture of $[(OC)_4Mn\{\mu\text{-}PR_2\}]_2$ and $[(OC)_3Mn(\mu\text{-}S{=}PR_2)]_3$ (R = Me, Et, *n*Pr, *n*Bu).[10]

(vi) Derivatization by reaction of the dinuclear complexes $[(OC)_4Mn\{\mu\text{-}PPhR\}]_2$ (R = Ph, Me) with HC≡CH and $H_2C{=}C{=}CH_2$ were also reported.[11]

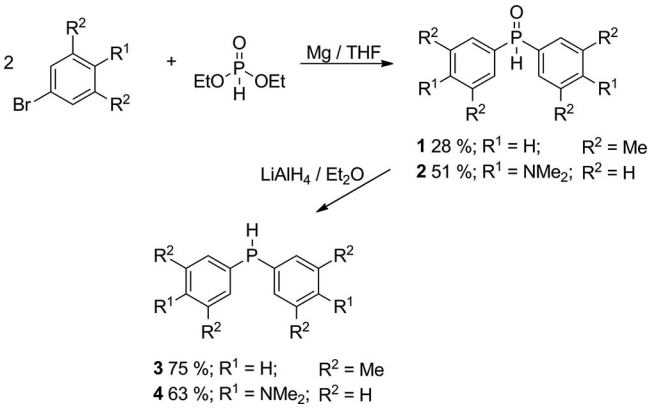
(vii) The reaction of $[(OC)_4Mn\{\mu\text{-}PHPh\}]_2$ with *n*-butyllithium and RX yielded the corresponding dinuclear complexes $[(OC)_4Mn\{\mu\text{-}PPhR\}]_2$ (R = Me, Et, *n*Pr, COMe, CH_2COMe, CO_2Et).[6,7]

Despite these early investigations, this substance class remained scarcely studied most probably due to the low yields and diverse side-products. In the frame of studies regarding the light-induced CO releasing molecules (photoCORMs)[12] for biological and medicinal applications, interest in this substance class arose because manganese(I) carbonyl complexes already proved to be an extremely valuable substance class for these applications. Early investigations clarified the first reaction step of light-triggered loss of one carbonyl ligand yielding $[\{(OC)_3Mn\}_2(\mu\text{-}CO)\{\mu\text{-}P(R)Aryl\}_2]$ with a Mn–Mn distance of 281.2(2) pm.[13] Applicability of these dinuclear complexes of the type $[(OC)_4Mn\{\mu\text{-}P(R)Aryl\}]_2$ for medicinal purposes requires solubility in aqueous solutions as well as non-toxicity of the complexes and their degradation products after CO liberation. In order to study the suitability of this substance class as photoCORMs, the P-bound substituents were varied in order to elucidate spectroscopic and structural properties. Recently, it has been demonstrated that manganese(I) carbonyls represent a promising substance class for medication of carbon monoxide. Thus, thiocarbamato[14] and thioacetato complexes[15] with the manganese(I) tetracarbonyl fragments (known as CORM-401 and CORM-371, respectively) have been tested in biological and medicinal tissues.

Results and Discussion

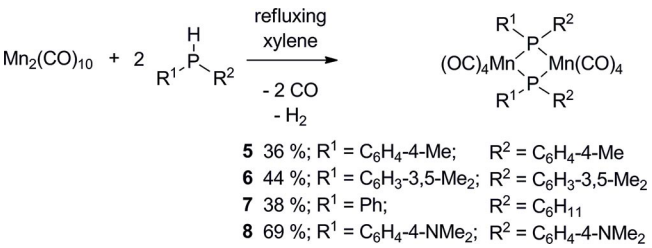
Synthesis

In analogy to earlier protocols,[16,17] the reaction of arylmagnesium bromide with diethyl phosphite yielded the corresponding secondary phosphane oxides as shown in Scheme 2. The reduction of these phosphane oxides succeeds with lithium aluminum hydride giving the corresponding secondary phosphanes.



Scheme 2. Synthesis of secondary phosphanes of the type HP(*R*)Aryl.

Metalation of these secondary phosphanes with $Mn_2(CO)_{10}$ in boiling xylene (mixture of isomers) till the evolution of gaseous carbon monoxide ceased gave the dinuclear complexes of the type $[(OC)_4Mn\{\mu\text{-}P(R)Aryl\}]_2$ with poor to moderate yields (Scheme 3) in analogy to an earlier procedure.[9] These manganese(I) complexes are only sparingly soluble or even nearly insoluble in hydrocarbons at room temperature. Therefore, no reliable NMR spectroscopic data were obtained for compound **6**.



Scheme 3. Synthesis of dinuclear complexes of the type $[(OC)_4Mn(\mu\text{-}PR^1R^2)]_2$.

The dinuclear nature of these complexes is evident from the coupling pattern of the $^{13}C\{^1H\}$ NMR resonances as shown in Figure 1 for complex **5**. The hyper fine structure of the signals appears as pseudo triplets of an $AA'X$ type spectrum due to the fact that the phosphorus nuclei are magnetically not equivalent. In agreement with an earlier report[18] it was not possible to detect the $^{13}C\{^1H\}$ NMR carbonyl resonances.

However, the complete interpretation of the $AA'X$ type coupling pattern was impossible because the $^{31}P\{^1H\}$ NMR resonances are broad (Figure 2) regardless of solvent, concentration, and substitution pattern of the aryl groups. For complex **7** transannular *syn*/*anti* isomerism should be expected, however, only one broad resonance was detected also for this derivative. In the $^{13}C\{^1H\}$ NMR spectrum the presence of both isomers leads to a double set of resonances. Due to the poor solubility, the carbonyl resonances have not been observed. Selected NMR parameters are summarized in Table 1. The chemical shifts of the $^{31}P\{^1H\}$ NMR resonances of $[(OC)_4Mn\{\mu\text{-}$

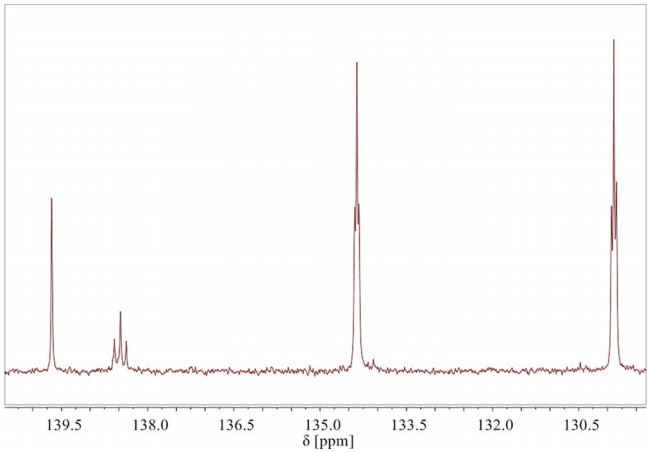


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **5** in [D_8]THF depicting the *AA′X* coupling pattern of the aryl carbon atoms.

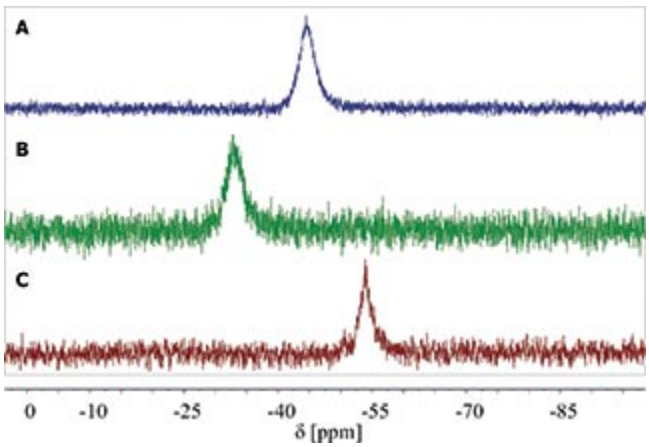


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **5** (A, [D_8]THF), **7** (B, CD_2Cl_2), and **8** (C, [D_8]THF) at room temperature showing the broadening of the resonances regardless of solvent and substitution pattern.

P*RR′*}]$_2$ significantly depend on the substitution pattern and are observed between approx. +100 (*R* = *R′* = alkyl)[10] and –200 ppm (*R* = *R′* = H).[5] The bis(aryl)phosphanides show chemical $^{31}P\{^1H\}$ NMR shifts around –50 ppm.

The stretching vibrations of the carbonyl ligands are also listed in Table 1. For [$(OC)_4Mn\{\mu\text{-}PPh_2\}]_2$ the carbonyl stretching modes were observed at 2053 [$A_1(1)$], 1992 [overlap of $A_1(2)$ and B_2], and 1957 cm^{-1} (B_1).[19] Substituents at the *P*-bound phenyl groups lead to an annihilation of the overlapping of the $A_1(2)$ and B_2 modes and hence, four stretching vibrations are observed. In complex **7** the phosphanide ligands carry a phenyl and a cyclo-hexyl group; therefore transannular *syn* and *anti* coordination is possible. Due to two possible isomers, five CO stretching modes are resolved in the IR spectrum.

The mass spectra of the complexes of the type [$(OC)_4Mn\{\mu$-P(*R*)Aryl}]$_2$ show the initial and step-wise loss of carbonyl ligands finally yielding the cations [$Mn\{\mu$-P(*R*)Aryl}]$_2^+$ ([M^+ – 8 CO]) which represent the most intense mass peak. For the derivatives **5** and **6**, also the monomeric [MnP(*R*)Aryl}]$^+$ cation was detected with substantial intensity. This monomerization behavior of the carbonyl-free cation of [$(OC)_4Mn\{\mu\text{-}PMe_2\}]_2$ was also observed earlier, however, in contrast to these findings, the cations, which arise from partial loss of carbonyl ligands, were not observed for this manganese(I) complex.[20]

Molecular Structures

The dinuclear manganese(I) complexes contain planar four-membered Mn_2P_2 rings with two carbonyl ligands *trans* to each other (marked as $C_{cis\text{-}P}$) and two carbonyls in *trans* position to the phosphorus atom (with the subscript $C_{trans\text{-}P}$). Selected structural parameters are summarized in Table 2. Compounds **5** and **8** are shown in Figure 3 and Figure 4, and complexes **6** and **7** are represented in Figures S1 and S2 (Supporting Information).

The Mn–P bond lengths vary between 235 and 241 pm mainly depending on the bulkiness of the P-bound substituents. Thus, the short bonds are observed to the bridging PH_2[21] and PMe_2[22] ligands, whereas the large Mn–P distances are enforced by the rather demanding P(*c*Hex)$_2$[9] and P(C_6H_3-3,5-Me_2)$_2$ groups. The shape of the central four-membered Mn_2P_2 ring also is influenced by the steric demand of the bridging phosphanide ligands with larger P–Mn–P bond angles for

Table 1. Selected spectroscopic parameters of carbonyl complexes of the type [$(OC)_4Mn(\mu\text{-}PR^1R^2)]_2$. Due to the fact that these complexes are only sparingly soluble, only the $^{31}P\{^1H\}$ NMR shifts are given. Furthermore, only the carbonyl stretching modes between 1900 and 2100 cm^{-1} are listed.

R^1 / R^2	Compound	$\delta(^{31}P)$ (solvent)	ν(CO)	Reference
Ph	–	–	2053, 1992, 1957	[3]
Me	–	106.00 ($CDCl_3$)	2046, 2016, 1984, 1962	[10]
Et	–	105.80 ($CDCl_3$)	2044, 1985, 1969, 1960	[10]
*n*Pr	–	105.60 ($CDCl_3$)	2041, 1977, 1962, 1958	[10]
*n*Bu	–	105.60 ($CDCl_3$)	2041, 1977, 1966, 1958	[10]
H	–	–194.00 (CD_2Cl_2)	2060, 1998, 1978, 1945	[4, 5]
*c*Hex / H	–	–88.00 ($CDCl_3$)	2049, 1999, 1981, 1968	[9]
Ph / H	–	–65.60 ($CDCl_3$)	2093, 2062, 2004, 1969	[6]
C_6H_4-4-Me	**5**	–44.51 ([D_8]THF)	2046, 1976, 1946, 1937	This work
C_6H_3-3,5-Me_2	**6**	–	2046, 1996, 1945, 1922	This work
Ph / *c*Hex	**7**	–32.16 (CD_2Cl_2)	2068, 2038, 1973, 1963, 1932	This work
C_6H_4-4-NMe_2	**8**	–53.89 ([D_8]THF)	2041, 1986, 1958, 1927	This work

Table 2. Selected structural parameters (average bond lengths /pm and angles /°) of carbonyl complexes of the type $[(OC)_4Mn(\mu\text{-}PR^1R^2)]_2$. The subscripts at the carbon atoms $C_{trans\text{-}P}$ and $C_{cis\text{-}P}$ characterize carbonyl ligands in *trans* and *cis* positions to the anions, respectively.

R^1 / R^2	Compound	Mn–$C_{trans\text{-}P}$	$C_{trans\text{-}P}$–O	Mn–$C_{cis\text{-}P}$	$C_{cis\text{-}P}$–O	Mn–P	P–Mn–P	Mn–P–Mn	Mn···Mn	Reference
H	–	183.1	113.0	184.1	113.5	235.1	76.1	103.9	370.3	[21]
Me	–	181.5	114.5	184.0	113.5	234.7	76.9	103.1	367.5	[22]
*c*Hex	–	–	–	–	–	241.1	78.6	101.4		[23]
*c*Hex / H	–	–	–	–	–	235.8	76.9	103.1		[23]
*n*Bu	–	184.8	115.2	185.3	114.9	239.8	77.2	102.8		[10]
Ph	–	182.4	113.6	184.5	113.6	238.8	78.7	101.2	369.0	[24]
Ph / H	–	182.1	114.1	184.2	113.4	235.6	77.0	103.1		[6]
Ph / C(O)Me	–	184	113	184	113	236.0	77.6	102.3		[6]
C_6H_4-4-Me	**5**	182.4	114.7	185.1	113.5	238.3	79.2	100.8	367.1	This work
C_6H_3-3,5-Me_2	**6**	181.3	114.8	185.4	113.1	240.7	81.6	98.4	364.3	This work
Ph / *c*Hex	**7**	182.6	114.4	185.0	113.9	239.0	78.3	101.7	370.6	This work
C_6H_4-4-NMe_2	**8**	182.6	114.3	184.6	113.4	239.5	79.1	100.9	370.1	This work

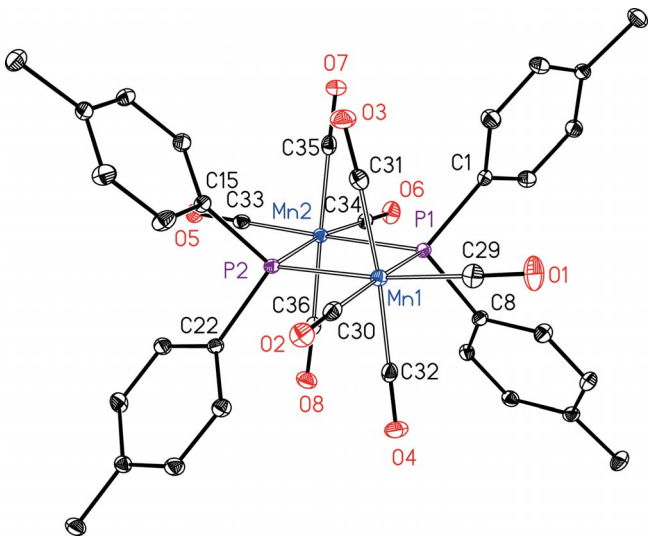


Figure 3. Molecular structure and numbering scheme of complex **5**. The ellipsoids represent a probability of 30, hydrogen atoms are omitted for clarity. Selected bond lengths /pm: Mn1–P1 238.91(7), Mn1–P2 237.51(7), Mn1–C29 183.0(3), Mn1–C30 181.7(2), Mn1–C31 185.1(3), Mn1–C32 185.1(3), Mn2–P1 238.43(7), Mn2–P2 238.37(7), Mn2–C33 182.3(3), Mn2–C34 183.4(2), Mn2–C35 185.2(3), Mn2–C36185.1(3), P1–C1 184.5(2), P1–C8 184.6(2), P2–C15 184.4(2), P2–C22 284.0(2). Bond angles /°: P1–Mn1–P2 79.23(2), P1–Mn2–P2 79.15(2), Mn1–P1–Mn2 100.55(3), Mn1–P2–Mn2 100.97(3), C1–P1–C8 97.5(1), C15–P2–C22 97.2(1).

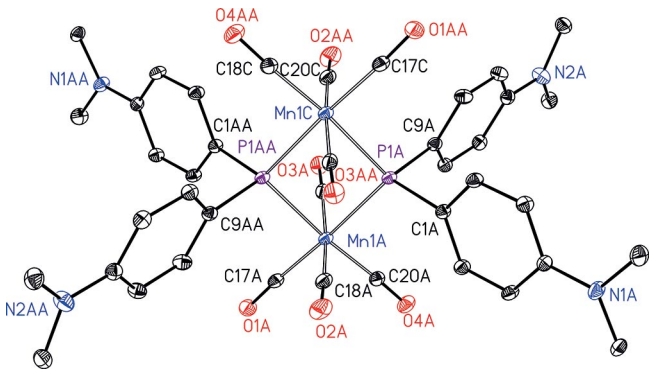


Figure 4. Molecular structure and numbering scheme of complex **8**. This compound crystallizes with two half molecules A and B in the asymmetric unit; only molecule A is depicted. A second letter A is added to the atoms generated by inversion symmetry. The ellipsoids represent a probability of 30 %, hydrogen atoms are omitted for clarity. Selected bond lengths /pm: Mn1A–P1A 238.96(6), Mn1A–P1AA 240.19(6), Mn1A–C17A 182.7(2), Mn1A–C18A 184.6(3), Mn1A–C19A 184.6(2), Mn1A–C20A 182.4(2), P1A–C1A 183.7(2), P1A–C9A 184.1(2). Bond angles /°: P1A–Mn1A–P1AA 79.14(2), C1A–P1A–C9A 99.2(1).

bulky phosphanides. A significantly larger average Mn–P bond length of 246.8 pm was observed for the trinuclear manganese complex $[\{(OC)_4Mn\}_2\{\mu\text{-}PPh_2\}\{\mu\text{-}P(Ph)Mn(CO)_5\}]$ to the bridging phosphorus atom bound to all three Mn atoms.[7]

The Mn–C distances to the carbonyl ligands expectedly depend on the *trans*-positioned moiety. The Mn–C bond lengths to the carbonyl groups in *trans* position to the bridging phosphanide are approximately 2 pm smaller than those of the carbonyl ligands in *cis* position to the phosphorus atoms due to an enhanced back donation from the metal into the π*(CO) orbitals. This charge transfer leads to a slight lengthening of the respective C–O bonds.

Conclusions

The synthesis of the dinuclear complexes of the type $[(OC)_4Mn(\mu\text{-}PRR')]_2$ [$R = R' = C_6H_4$-4-Me (**5**), C_6H_3-3,5-Me_2 (**6**), R/R' = Ph/*c*Hex (**7**), $R = R' = C_6H_4$-4-NMe_2 (**8**)] succeeds via the metalation of the appropriate secondary phosphanes HP*RR′* (*R* = aryl, *R′* = aryl, *c*Hex) with $Mn_2(CO)_{10}$ in boiling xylene (mixture of isomers) only with poor to moderate yields. These complexes are only sparingly soluble in hydrocarbons and this fact hampered the measurements of NMR spectra. Due to the insolubility of these manganese(I) complexes in ethereal and aqueous solutions they are inappropriate for biological and medicinal applications.

The yellow manganese(I) carbonyl phosphanides can be recrystallized from toluene, yielding single crystals suitable for X-ray diffraction experiments. The molecular structures contain central planar Mn_2P_2 rings. Due to the *trans* effect, the carbonyl ligands *trans* to the phosphorus atoms show a

stronger charge transfer from the metal into the π*(CO) orbital leading to smaller Mn–C bond lengths and slightly larger C–O distances than observed for carbonyl ligands *trans* arranged to each other. These complexes are significantly more stable than the isostructural thiolates of the type $[(OC)_4Mn(\mu\text{-}SR)]_2$, which degrade under liberation of carbon monoxide to tetranuclear $[(OC)_3Mn(\mu_3\text{-}SR)]_4$.[1]

Experimental Section

General: All manipulations were carried out in an inert nitrogen atmosphere using standard Schlenk techniques. The solvents were purified and dried by standard techniques prior to use. The yields given are not optimized. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with Bruker AC 200, AC 400, and AC 600 spectrometers. Chemical shifts are reported in parts per million. [D$_8$]THF was dried with sodium. Chemicals and solvents were commercially available and were used as received without further purification. The synthesis of phosphanes that were not purchased, are described in the Supporting Information.

Synthesis of $\{(CO)_4Mn[P(C_6H_4\text{-}4\text{-}Me)_2]\}_2$ (5): $Mn_2(CO)_{10}$ (230 mg, 0.59 mmol) was suspended in xylene (20 mL, mixture of isomers). In another flask bis(*p*-tolyl)phosphane (280 mg, 1.31 mmol) was dissolved in xylene (30 mL) and transferred at once to the $Mn_2(CO)_{10}$ suspension. The reaction was heated to reflux for 4 h until gas evolution ceased. After the reaction mixture was allowed to cool to room temperature, CO was bubbled through the solution for 2 min. Reduction of the volume under reduced pressure yielded a yellow solid. This precipitate was suspended in toluene (2 mL), filtered, washed with toluene (another 2 mL) and dried in vacuo. Recrystallization from toluene gave single crystals suitable for X-ray diffraction studies. Yield: 160 mg (0.21 mmol, 36 %). **^{1}H NMR** (400.075 MHz, [D$_8$]THF): δ = 7.64 (m, 8 H), 7.16 (m, 8 H), 2.29 (s, 12 H). ^{31}P NMR (161.953 MHz, [D$_8$]THF): δ = –44.5 (s). **^{13}C{^{1}H} NMR** (101.599 MHz, [D$_8$]THF): δ = 139.3 (s), 138.1 (AA'X type), 134.0 (AA'X type), 129.5 (AA'X type), 20.8 (s). **MS** (DEI): *m*/*z* (%) = 732 [M$^+$ – CO] (24), 648 [M$^+$ – 4 CO] (41), 536 [M$^+$ – 8 CO] (100), 481 (22), 299 (53), 268 [M$^+$ – 8 CO]$_{0.5}$ (50), 237 (40), 211 (53), 146 (29), 55 (44). **IR** (neat solid): $\tilde{\nu}$ = 2046 (m), 1976 (s), 1946 (m), 1937 (s), 1495 (w), 1447 (w), 1394 (w), 1306 (w), 1263 (w), 1190 (w), 1081 (w), 1041 (w), 1016 (w), 802 (w), 542 (w), 513 (m), 505 (s), 488 (m), 475 (m), 447 (m), 434 (m), 416 (m) cm^{-1}. $C_{36}H_{28}Mn_2O_8P_2$ (760.43): calcd. C 56.86, H 3.71 %; found: C 56.48, H 3.80 %. M.p.: 479 K (dec.).

Synthesis of $\{(CO)_4Mn[P(C_6H_3\text{-}3,5\text{-}Me_2)_2]\}_2$ (6): $Mn_2(CO)_{10}$ (315 mg, 0.81 mmol) was suspended in xylene (20 mL, mixture of isomers). In another flask bis(3,5-dimethylphenyl)phosphane (388 mg, 1.60 mmol) was dissolved in xylene (5.4 mL) and transferred at once to the $Mn_2(CO)_{10}$ suspension. The reaction was heated to reflux for 4 h until gas evolution ceased. While the reaction mixture was allowed to cool to room temperature, a yellow solid formed. The precipitate was collected, washed with cold xylene (2 mL) and dried in vacuo. The yellow residue was recrystallized from toluene. Yield: 290 mg (0.36 mmol, 44 %). **MS** (DEI): *m*/*z* (%) = 788 [M$^+$– CO] (27), 704 [M$^+$– 4 CO] (84), 676 [M$^+$– 5 CO] (9), 648 [M$^+$–6 CO] (43), 620 [M$^+$– 7 CO] (4), 592 [M$^+$– 8 CO] (100), 537 [M$^+$– 8 CO - Mn] (22), 482 [$((Me_2C_6H_3)_2P)_2^+$] (5), 327 [$MnP_2(C_6H_3Me_2)_2^+$] (71), 296 [$MnP(C_6H_3Me_2)_2^+$] (100), 241 [$P(C_6H_3Me_2)_2^+$] (16). **IR** (neat solid): $\tilde{\nu}$ = 2918(w), 2851 (w), 2047 (w), 1997 (w), 1946 (m), 1923 (m), 1894 (w), 1842 (w), 1799 (w), 1768 (w), 1747 (w), 1731 (w), 1714 (w), 1694 (w), 1681 (w), 1667 (w), 1660 (w), 1651 (w), 1644 (w), 1633 (w), 1614 (w), 1599 (w), 1574 (w), 1556 (w), 1538 (w), 1515 (w), 1504 (w), 1495 (w), 1485 (w), 1463 (w), 1454 (w), 1434 (w), 1405 (w), 1373 (w), 1299 (w), 1259 (w), 1117 (w), 1036 (w), 993 (w), 898 (w), 875 (w), 829 (w), 799 (w), 693 (w), 683 (w), 555 (m), 515 (m), 496 (m), 475 (m), 432 (w), 406 (w) cm^{-1}. $C_{40}H_{36}Mn_2O_8P_2$, 815.53): calcd. C 58.84, H 4.44 %; found: C 59.38, H 4.71 %. M.p.: 509 K (dec.).

Synthesis of $\{(CO)_4Mn[P(Ph)(cHex)]\}_2$ (7): $Mn_2(CO)_{10}$ (753 mg, 1.89 mmol) was suspended in xylene (20 mL, mixture of isomers). In another flask (cyclo-hexyl)phenylphosphane (798 mg, 4.15 mmol) was dissolved in xylene (30 mL) and transferred at once to the $Mn_2(CO)_{10}$ suspension. The reaction was heated to reflux for 4 h until gas evolution ceased. While the reaction mixture was allowed to cool to room temp., a yellow solid precipitated. Afterwards CO was bubbled through the solution for 2 min. The precipitate was collected, washed with *n*-hexane (3 mL) and dried in vacuo. Yield: 518 mg (0.72 mmol, 38 %). **^{1}H NMR** (400.075 MHz, CD_2Cl_2): δ = 7.88–7.73 (m, 4 H), 7.60–7.29 (m, 6 H), 2.34–2.15 (m, 6 H), 1.83–1.73 (m, 4 H), 1.61–1.51 (m, 4 H), 1.44–1.29 (m, 8 H). **^{31}P NMR** (161.953 MHz, CD_2Cl_2): δ = –32.2 (s). **^{13}C{^{1}H} NMR** (100.599 MHz, CD_2Cl_2): δ = 136.1 (AA'X type), 135.8 (AA'X type), 134.3 (AA'X type), 129.6 (s), 129.5 (s), 128.0 (m), 43.5 (AA'X type), 43.2 (AA'X type), 30.5 (AA'X type), 30.3 (AA'X type), 28.0 (AA'X type), 27.9 (AA'X type), 26.0 (s), 25.9 (s). **MS** (DEI): *m*/*z* (%) = 688 [M$^+$ – CO] (32), 604 [M$^+$ – 4 CO] (60), 492 [M$^+$ – 8 CO] (100). **IR** (neat solid): $\tilde{\nu}$ = 3062 (w), 2931 (w), 2857 (w), 2068 (w), 2038 (m), 1973 (s), 1963 (s), 1932 (vs), 1477 (w), 1450 (w), 1431 (w), 1336 (w), 1295 (w), 1265 (w), 1202 (w), 1173 (w), 1112 (w), 1080 (w), 1048 (w), 1001 (w), 915 (w), 890 (w), 850 (w), 819 (w), 740 (m), 722 (w), 696 (m), 551 (m), 524 (m), 499 (s), 484 (s), 447 (s), 418 (s) cm^{-1}. $C_{32}H_{32}Mn_2O_8P_2$, 716.42): calcd. C 53.65, H 4.50 %; found: C 53.32, H 4.45 %. M.p.: 463 K (dec.).

Synthesis of $\{(CO)_4Mn[P(C_6H_4\text{-}4\text{-}NMe_2)_2]\}_2$ (8): $Mn_2(CO)_{10}$ (249 mg, 0.62 mmol) was suspended in xylene (5 mL, mixture of isomers). In another flask bis(4-dimethylaminophenyl)phosphane (350 mg, 1.29 mmol) was dissolved in xylene (20 mL) and transferred at once to the $Mn_2(CO)_{10}$ suspension. The reaction was heated to reflux for 4 h until gas evolution ceased. During this time, a yellow solid precipitated. After the reaction mixture was allowed to cool to room temperature CO was bubbled through the solution for 2 min. The precipitate was collected, washed twice with xylene (5 mL) and dried in vacuo. The yellow residue was recrystallized from THF. Yield: 378 mg (0.43 mmol, 69 %). **^{1}H NMR** (400.075 MHz, [D$_8$]THF): δ = 7.60–7.53 (m, 8 H), 6.66 (m, 8 H), 2.92 (s, 24 H). **^{31}P NMR** (161.953 MHz, [D$_8$]THF): δ = –53.9 (s). **^{13}C{^{1}H} NMR** (100.599 MHz, [D$_8$]THF): δ = 151.1 (s), 135.1 (AA'X type), 130.6 (AA'X type), 112.2 (AA'X type), 40.1 (s). **MS** (Micro-ESI pos. in THF and methanol): *m*/*z* (%) = 876.9 [M$^+$ + H] (75), 848.9 [M$^+$ + H - CO] (26), 820.9 [M$^+$ + H - 2 CO] (32), 699.1 (37), 629.2 (62), 599.1 (100), 199.0 (43). **IR** (neat solid): $\tilde{\nu}$ = 3088 (w), 2896 (w), 2857 (w), 2812 (w), 2041 (m), 1986 (s), 1958 (s), 1927 (s), 1593 (m), 1545 (w), 1508 (m), 1443 (m), 1420 (w), 1359 (m), 1318 (w), 1284 (w), 1231 (m), 1202 (m), 1173 (w), 1121 (w), 1086 (m), 998 (w), 948 (m), 931 (w), 804 (m), 777 (w), 764 (w), 751 (w), 718 (w), 694 (w), 650 (s), 633 (s), 550 (m), 529 (m), 516 (s), 493 (m), 432 (m), 417 (m), 407 (m) cm^{-1}. $C_{40}H_{40}Mn_2N_4O_8P_2$, 876.59): calcd. C 54.81, H 4.60, N 6.39 %; found: C 54.69, H 4.95, N 6.13 %. M.p.: 458 K (dec.).

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on

Table 3. Crystal data and refinement details for the X-ray structure determinations for compounds **5**–**8**.

	5	**6**	**7**	**8**
Formula	$C_{36}H_{28}Mn_2O_8P_2$	$C_{40}H_{36}Mn_2O_8P_2$[*]	$C_{32}H_{32}Mn_2O_8P_2$	$C_{48}H_{50}Mn_2N_4O_8P_2$
Fw /g·mol^{-1}	760.40	816.51[*]	716.40	982.74
T /°C	–140(2)	–140(2)	–140(2)	–140(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/m$	$P\bar{1}$
a /Å	10.5614(2)	8.8628(2)	13.6298(15)	13.0615(2)
b /Å	18.8623(3)	11.6388(3)	11.5464(13)	13.6658(3)
c /Å	17.4536(3)	11.7388(3)	11.8367(14)	14.1632(3)
α /°	90	105.573(1)	90	82.253(1)
β /°	103.412(1)	111.788(1)	121.800(6)	66.658(1)
γ /°	90	95.672(2)	90	86.432(1)
V /Å^3	3382.14(10)	1056.10(5)	1583.2(3)	2299.87(8)
Z	4	1	2	2
ρ /g·cm^{-3}	1.493	1.284[a)]	1.503	1.419
μ /cm^{-1}	8.93	7.2[a)]	9.49	6.77
Measured data	20263	6670	4251	13937
Data with $I > 2\sigma(I)$	6380	4244	1650	9373
Unique data (R_{int})	7734/0.0391	4598/0.0149	1854/0.0481	10345/0.0215
wR_2 (all data, on F^2)[b)]	0.0870	0.1305	0.1221	0.1103
R_1 [$I > 2\sigma(I)$][b)]	0.0407	0.0478	0.0503	0.0451
s[c)]	1.080	1.100	1.165	1.074
Res. dens./e·Å^{-3}	0.405/–0.366	0.799/–0.598	0.625/–0.415	0.974/–0.541
Absorpt method	multi-scan	multi-scan	multi-scan	multi-scan
Absorpt corr $T_{min}/_{max}$	0.6382/0.7456	0.7123/0.7456	0.7087/0.7456	0.6875/0.7456

a) These parameters do not contain the contribution of the disordered solvent. b) Definition of the R indices: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2)+(aP)^2+bP$; $P = [2F_c^2+\mathrm{Max}(F_o^2]/3$. c) $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

a semi-empirical basis using multiple-scans.[25–27] The structures were solved by direct methods (SHELXS)[28] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[28] All hydrogen atoms bound to the compounds **5** and the hydrogen atoms of the phenyl groups of **8** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen and non-disordered atoms were refined anisotropically.[28] The crystal of **6** contains large voids, filled with disordered solvent molecules. The sizes of the voids are 178 Å^3 per unit cell. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON[29] resulting in 98 electrons per unit cell. The crystals of complex **7** contain the different *syn* and *anti* isomers. This fact causes a disordering of the *P*-bound phenyl and cyclohexyl groups. This disordering could be resolved for a part of the molecule. Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1451187 for **5**, CCDC-1451188 for **6**, CCDC-1451189 for **7**, and CCDC-1451190 for **8** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Preparative details of **1** to **4** and structure representations of the dinuclear manganese(I) complexes **6** and **7**.

Acknowledgements

The authors gratefully acknowledge the Deutsche Forschungsgemeinschaft (DFG, Bonn, Germany) for generously funding this project in the frame of the collaborative research group FOR 1738. Support of the Fonds der Chemischen Industrie (Frankfurt/Main, Germany) is also acknowledged. Infrastructure of the Institute of Inorganic and Analytical Chemistry of the Friedrich Schiller University Jena was partially provided by the EU (European Regional Development Fund, EFRE). Some of the presented results are taken from the bachelor thesis of *S.B.*

References

[1] a) R. Mede, V. P. Lorett-Velàsquez, M. Klein, H. Görls, M. Schmitt, G. Gessner, S. H. Heinemann, J. Popp, M. Westerhausen, *Dalton Trans.* **2015**, *44*, 3020–3033; b) R. Mede, M. Klein, R. A. Claus, S. Krieck, S. Quickert, H. Görls, U. Neugebauer, M. Schmitt, G. Gessner, S. H. Heinemann, J. Popp, M. Bauer, M. Westerhausen, *Inorg. Chem.* **2016**, *55*, 104–113.
[2] M. L. H. Green, J. T. Moelwyn-Hughes, *Z. Naturforsch.* **1962**, *17b*, 783–784.
[3] a) R. G. Hayter, *J. Am. Chem. Soc.* **1964**, *86*, 823–828; b) W. Hieber, R. Kummer, *Z. Naturforsch.* **1965**, *20b*, 271.
[4] a) H. Schäfer, J. Zipfel, B. Gutekunst, U. Lemmert, *Z. Anorg. Allg. Chem.* **1985**, *529*, 157–172; b) H. Schäfer, J. Zipfel, B. Migula, D. Binder, *Z. Anorg. Allg. Chem.* **1983**, *501*, 111–120.
[5] E. W. Abel, I. H. Sabherwal, *J. Organomet. Chem.* **1967**, *10*, 491–494.
[6] M. P. Brown, J. Buckett, M. M. Harding, R. M. Lynden-Bell, M. J. Mays, K. W. Woulfe, *J. Chem. Soc., Dalton Trans.* **1991**, 3097–3102.
[7] L. Manojlovic-Muir, K. W. Muir, M. C. Jennings, M. J. Mays, G. A. Solan, K. W. Woulfe, *J. Organomet. Chem.* **1995**, *491*, 255–262.
[8] U. Flörke, H.-J. Haupt, *Acta Crystallogr., Sect. C* **1993**, *49*, 533–535.
[9] H.-J. Haupt, M. Schwefer, U. Flörke, *Inorg. Chem.* **1995**, *34*, 292–297.
[10] G. Hogarth, F. Sarýkahya, O. S. Þentürk, *Polyhedron* **2002**, *21*, 791–795.

[11] L. Manojlović-Muir, M. J. Mays, K. W. Muir, K. W. Woulfe, *J. Chem. Soc., Dalton Trans.* **1992**, 1531–1538.
[12] For recent reviews on metal-based CORMs see, for example: a) X. Ji, K. Damera, Y. Zheng, B. Yu, L. E. Otterbein, B. Wang, *J. Pharmaceut. Sci.* **2016**, *105*, 406–416; b) J. Marhenke, K. Trevino, C. Works, *Coord. Chem. Rev.* **2016**, *306*, 533–543; c) H. Inaba, K. Fujita, T. Ueno, *Biomaterials Sci.* **2015**, *3*, 1423–1438; d) U. Schatzschneider, *Brit. J. Pharmacol.* **2015**, *172*, 1638–1650; e) P. V. Simpson, U. Schatzschneider, *Inorg. Chem. Biol.* **2014**, 309–339; f) S. H. Heinemann, T. Hoshi, M. Westerhausen, A. Schiller, *Chem. Commun.* **2014**, *50*, 3644–3660; g) S. García-Gallego, G. J. L. Bernardes, *Angew. Chem. Int. Ed.* **2014**, *53*, 9712–9721; h) M. A. Gonzales, P. K. Mascharak, *J. Inorg. Biochem.* **2014**, *133*, 127–135; i) F. Zobi, *Future Med. Chem.* **2013**, *5*, 175–188; j) C. C. Romão, W. A. Blättler, J. D. Seixas, G. J. L. Bernardes, *Chem. Soc. Rev.* **2012**, *41*, 3571–3583; k) R. D. Rimmer, A. E. Pierri, P. C. Ford, *Coord. Chem. Rev.* **2012**, *256*, 1509–1519; l) U. Schatzschneider, *Inorg. Chim. Acta* **2011**, *374*, 19–23; m) U. Schatzschneider, *Eur. J. Inorg. Chem.* **2010**, 1451–1467; n) R. Motterlini, L. E. Otterbein, *Nat. Rev.* **2010**, *9*, 728–743; o) B. E. Mann, *Top. Organomet. Chem.* **2010**, *32*, 247–285.
[13] T. Kawamura, T. Sowa, T. Yonezawa, T. Yamabe, H. Masuda, T. Taga, K. Machida, *J. Organomet. Chem.* **1984**, *276*, C10-C12.
[14] a) S. H. Crook, B. E. Mann, A. J. H. M. Meijer, H. Adams, P. Sawle, D. Scapens, R. Motterlini, *Dalton Trans.* **2011**, *40*, 4230–4235; b) P. Kaczara, R. Motterlini, G. M. Rosen, B. Augustynek, P. Bednarczyk, A. Szewczyk, R. Foresti, S. Chlopicki, *Biochim. Biophys. Acta* **2015**, *1847*, 1297–1309; c) S. Fayad-Kobeissi, J. Ratovonantenaina, H. Dabiré, J. L. Wilson, A. M. Rodriguez, A. Berdeaux, J.-L. Dubois-Randé, B. E. Mann, R. Motterlini, R. Foresti, *Biochem. Pharmacol.* **2016**, *102*, 64–77.
[15] M. Desmard, R. Foresti, D. Morin, M. Dagouassat, A. Berdeaux, E. Denamur, S. H. Crook, B. E. Mann, D. Scarpens, P. Montravers, J. Boczkowski, R. Motterlini, *Antioxid. Redox Signal.* **2012**, *16*, 153–163.
[16] N. Giri, W. Clegg, R. W. Harrington, P. N. Horton, M. B. Hursthouse, S. L. James, *Chem. Commun.* **2012**, *48*, 4061–4063.
[17] C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 4277–4280.
[18] H. Zhang, X. Ye, D. Wang, G. Liu, *Prog. Nat. Sci.* **1998**, *8*, 568–572.
[19] E. W. Abel, J. Dalton, I. Paul, J. G. Smith, F. G. A. Stone, *J. Chem. Soc. A* **1968**, 1203–1208.
[20] B. F. G. Johnson, J. Lewis, J. M. Wilson, D. T. Thompson, *J. Chem. Soc. A* **1967**, 1445–1448.
[21] B. Deppisch, H. Schäfer, D. Binder, W. Leske, *Z. Anorg. Allg. Chem.* **1984**, *519*, 53–66.
[22] H. Vahrenkamp, *Chem. Ber.* **1978**, *111*, 3472–3483.
[23] U. Flörke, H.-J. Haupt, *Acta Crystallogr., Sect. C* **1993**, *49*, 533–535.
[24] H. Masuda, T. Taga, K. Machida, T. Kawamura, *J. Organomet. Chem.* **1987**, *331*, 239–245.
[25] *COLLECT*, Data Collection Software; Nonius B. V., Delft, The Netherlands, **1998**.
[26] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected*, in: *Oscillation Mode*, (Eds.: C. W. Carter, R. M. Sweet), *Methods in Enzymology*, vol. 276, *Macromolecular Crystallography, Part A*, pp. 307–326, Academic Press, London, **1997**.
[27] *SADABS 2.10*, Bruker-AXS Inc., Madison, WI, USA, **2002**.
[28] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[29] A. L. Spek, *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.

Received: February 4, 2016
Published Online: March 23, 2016

