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# The synthesis of $[(\eta^6\text{-Flu}^*\text{H})\text{Mn(CO)}_3]\text{PF}_6$, and its deprotonation to yield a novel coordination mode of fluorene

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**Abstract**

The synthesis of $[(\eta^6\text{-Flu}^*\text{H})\text{Mn(CO)}_3]\text{PF}_6$ is reported. The complex may be deprotonated to give a neutral zwitterionic complex. Instead of deprotonation at the 9-position, as seen in the non-methylated complex, deprotonation of a ring methyl is observed. This yields a previously unknown coordination mode of fluorene, and may be explained on both electronic and steric grounds.


*Keywords:* Fluorene; Nonamethylfluorene; Arene manganese tricarbonyl; Deprotonation

## 1. Introduction

It has long been known that the reactivity of arenes coordinated to metal fragments is greatly enhanced in comparison to the free arene molecule. The majority of examples in the literature refer to $\text{AreneCr(CO)}_3$ derivatives, and these have found many uses in organic synthesis, especially in the highly selective preparation of substituted cyclohexadienes [1–4]. An increasing number of Arene $\text{Mn(CO)}_3^+$ complexes have now been isolated, and their use in both the synthesis of useful organic compounds and other organometallic complexes is beginning to be exploited [2,5,6].

The complex $[(\eta^6\text{-FluH})\text{Mn(CO)}_3]^+$ (FluH = 9*H*-fluorene) has been known since 1976 [7]. Many studies have focussed on the deprotonation of this complex at the 9-position of the ligand, and the kinetics and mechanism of the subsequent equilibrium between the $\eta^6$-bound and the $\eta^5$-bound $\text{Mn(CO)}_3^+$ fragment (Fig. 1) [8–12].

With the goal of examining a similar haptotropic shift, the fully methylated complex $[(\eta^6\text{-Flu}^*\text{H})\text{Mn(CO)}_3]\text{PF}_6$ ($\text{Flu}^*\text{H}$ = 1,2,3,4,5,6,7,8,9-nonamethyl-9*H*-fluorene), was synthesised, and subjected to deprotonation. However, unlike the non-methylated complex, deprotonation at the 9-position does not occur. Instead, deprotonation of one of the methyl groups at the rear of the molecule is seen. The characterisation of this complex indicates a previously unseen coordination mode of the fluorene ligand.

## 2. Experimental

All manipulations were carried out under $N_2$ using Schlenk techniques. Solvents were dried using standard drying agents, and were thoroughly degassed before use. Deuterated NMR solvents were dried and degassed by three freeze–pump–thaw cycles before use. Solution NMR data were collected on a Varian Venus 300 MHz at room temperature, $^1$H NMR at 300 MHz and $^{13}$C NMR at 75 MHz. Mass spectrometry was carried out by the mass spectrometry service, Chemistry Research Laboratory, University of Oxford. IR spectra were obtained on a Perkin–Elmer Paragon 1000 machine as solutions in $CH_2Cl_2$, using a KBr cell at a resolution of $\pm 1$ cm$^{-1}$. Crystals were mounted on a glass fibre with perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD

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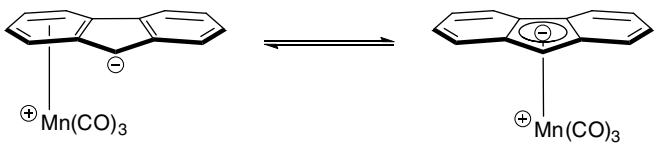


Fig. 1. Schematic view of the haptotropic equilibrium for the deprotonated form of $[(\eta^6\text{-FluH})Mn(CO)_3]^+$.

diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package. The structure was then solved using the direct-methods program SIR 92, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite [13–15]. Flu*H was synthesised via the literature method [16].

### 2.1. $[(\eta^6\text{-Flu}^*H)Mn(CO)_3]PF_6$ (1)

This complex was synthesised via the method of Treichel and Johnson [12]. $BrMn(CO)_5$ (0.47 g, $1.71 \times 10^{-3}$ mol), $AlCl_3$ (1.14 g, $8.55 \times 10^{-3}$ mol) and Flu*H (0.5 g, $1.71 \times 10^{-3}$ mol) were combined in a Schlenk tube in the glove box. 25 ml dry hexane was added, and the mixture refluxed overnight. On cooling to room temperature, 40 ml water was added to the red solution, giving a yellow solution and evolution of HCl gas. The solution was filtered, the layers separated, and the aqueous layer washed several times with pentane until the washings ran clear. An excess of $NH_4PF_6$ (ca. 3 g) was added in one portion, and a yellow precipitate formed immediately. This was collected by filtration, dried in a desiccator, and transferred to the glove box for long term storage. The complex was isolated as $[(\eta^6\text{-Flu}^*H)Mn(CO)_3]PF_6 \cdot 0.5CH_2Cl_2$. Yield: 0.45 g, 42.70%. $^1$H NMR ($CD_2Cl_2$) $\delta$ (ppm): 1.49 (d, 3H, 9-Me, $J = 6$ Hz), 2.31, 2.33, 2.38, 2.43, 2.48, 2.51, 2.65, 2.69 (all s, 3H, Me), 4.29 (q, 1H, 9-*H*, $J = 6$ Hz). $^{13}$C NMR ($CD_2Cl_2$) $\delta$ (ppm): 16.2, 16.7, 17.2, 17.6, 19.0, 21.7, 22.3, 22.9 (ring Me), 43.0 (9-C), 100–140 (Ar Flu*H, very weak). HRMS ($LCT^+$): 431.14 ($M^+$, difference from calculated +2.7 ppm), 347.16 ($M^+-3CO$), fragmentation due to methyl loss. *Anal*. Calc for $C_{25.5}H_{29}O_3MnPF_6Cl$: C, 49.49; H, 4.72. Found: C, 49.19; H, 4.92%. IR ($CH_2Cl_2$) cm$^{-1}$: 1999.7, 2057.7.

### 2.2. Deprotonation of $[(\eta^6\text{-Flu}^*H)Mn(CO)_3]PF_6$ (2)

$^t$BuOK (0.06 g, $5.21 \times 10^{-4}$ mol) and $[(\eta^6\text{-Flu}^*H)Mn(CO)_3]PF_6$ (0.1 g, $1.74 \times 10^{-4}$ mol) were combined in a Schlenk tube. On addition of 15 ml $CH_2Cl_2$, the colour immediately became dark orange. After 15 min, the $CH_2Cl_2$ was removed under vacuum, and the orange residue extracted with 50 ml hexane, and filtered into a new Schlenk. The solution was reduced to a minimum volume, and slowly cooled to −80 °C to give a dark orange powder. Yield: 0.05 g, 66.80%. Single crystals suitable for X-ray diffraction were obtained via the slow evaporation of a $C_6D_6$ solution of **2**. $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 1.27 (d, 3H 9-Me, $J = 7.2$ Hz), 1.64, 1.68, 1.96, 1.99, (all s, 3H, Me), 2.09 (s, 6H, Me), 2.68 (s, 3H, Me), 3.75 (q, 1H, 9-*H*, $J = 7.2$ Hz) 4.27 (s, 2H, $CH_2$). $^{13}$C NMR ($C_6D_6$)$\delta$ (ppm): 15.3, 15.7, 16.0, 16.1, 16.8, 18.2 (ring Me), 19.1 (9-Me), 19.5 (ring Me), 42.9 (9-C), 78.5, 79.5, 86.7 (complexed ring C), 92.9 ($CH_2$), 107.8, 123.6 (complexed ring C), 128.6, 129.9, 133.5, 135.6, 137.7, 142.5 (uncomplexed ring C), 143.4 ($CH_2 = C$ ring C). HRMS (EI): 430.1334 ($M^+$, difference from calculated −1.6 ppm), fragmentation due to loss of Me. IR ($CH_2Cl_2$) cm$^{-1}$: 1912.3, 1927.8, 2000.3. Due to the air sensitivity of this complex, satisfactory elemental analysis could not be obtained.

## 3. Results and discussion

The reaction of stoichiometric amount of $BrMn(CO)_5$, Flu*H and an excess of $AlCl_3$ produces $[(\eta^6\text{-Flu}^*H)Mn(CO)_3]PF_6$ (**1**) in approximately 45% yield (Fig. 2).

Compound **1** is isolated as an air stable, yellow solid and is highly soluble in dichloromethane. NMR and MS data confirm that only one $Mn(CO)_3^+$ unit is bound to the ligand. As with many $AreneMn(CO)_3$ complexes, rapid decomposition is seen in solvents such as THF and acetonitrile, yielding the free ligand and unidentified metal containing species. This instability is generally ascribed to solvent coordination and subsequent ligand loss.[17] Although relatively stable in air, **1** was stored in the glove box under $N_2$ for long periods with no apparent signs of decomposition.

IR analysis of **1** indicates that the methyl groups of the ligand exert a significant electronic influence over the Mn centre. This is shown by a movement of the CO frequencies to 7 cm$^{-1}$ lower wavenumber than in the non-methylated complex [12]. This is a similar shift to that seen when benzene is replaced by hexamethylbenzene in the analogous complexes, and is further proof that the Flu*H ligand is highly electron donating.

When **1** is reacted with $^t$BuOK in $CH_2Cl_2$, an immediate colour change from yellow to dark orange is seen. On removal of the solvent and hexane extraction, **2** is isolated as dark yellow blocks. **2** is sensitive to air and moisture, gradually becoming yellow on prolonged exposure. NMR analysis indicates decomposition back to the parent complex **1** is occurring. The complex is highly soluble in hydrocarbon solvents, and exhibits no signs of decomposition in these solvents, even at elevated temperatures. Initially it was believed that deprotonation at the 9-position had occurred, as in the non-methylated analogue. However, $^1$H NMR studies showed that this deprotonation had not occurred, as evidenced by the quartet at 3.75 ppm and the doublet at 1.27 ppm, indicative of the 9-position Me and H substituents. The $^1$H NMR spectrum also showed an unexpected resonance at 4.27 ppm, integrating to 2H, and apparently corresponding to an exocyclic double bond. A ROESY analysis of the molecule indicated that the dou-

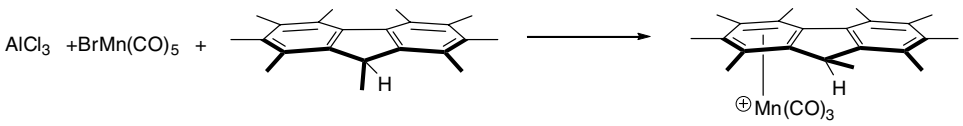


Fig. 2. Synthesis of $[(\eta^6\text{-Flu}^*\text{H})\text{Mn(CO)}_3]\text{PF}_6$ (**1**).

ble bond was located at the rear of the molecule at the 4-position of the fluorene skeleton, shown in Fig. 3.

In order to confirm the structure, an X-ray diffraction study of **2** was performed. Crystals were grown by the slow evaporation of a $C_6D_6$ solution under an $N_2$ atmosphere. The X-ray structure confirmed the presence of the double bond at the rear of the molecule. Two views of this structure are shown in Figs. 4a and 4b.

As can be seen from Fig. 4, the $Mn(CO)_3^+$ fragment is bound $\eta^5$ to the Flu*H ligand. This implies a cyclohexadienyl structure at the ligand, and further evidence for this is given by the IR data, which show the CO frequencies moved to approximately 100 $cm^{-1}$ lower wavenumber. Three IR bands are observed, indicating a reduction of symmetry at the Mn, on binding to a cyclohexadienyl fragment. This shift to lower wavenumber is indicative of an increase in electron density at the metal, implying it is bound to a negatively charged ligand. As shown by the crystal structure, the $Mn(CO)_3^+$ moiety is only coordinated to five of the six carbon atoms in the arene ring, with the

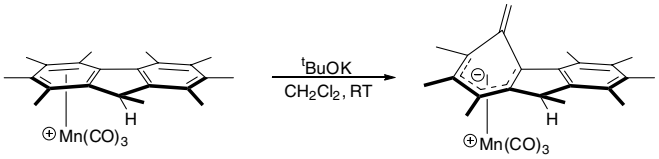


Fig. 3. Deprotonation of **1** to form **2**.

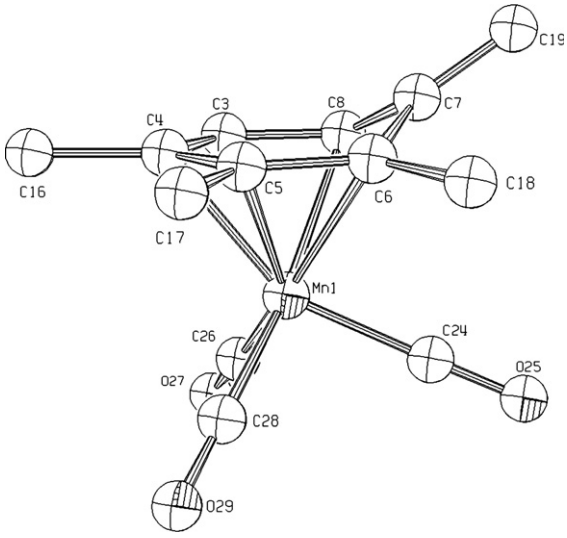


Fig. 4b. Diagram of metal binding in **2**, only the ring bound to the metal shown. C19 and C7 significantly bent out of plane. Hydrogen atoms omitted for clarity, thermal ellipsoids at 50%.

remaining carbon significantly displaced from the metal atom to form a double bond with its Me substituent. This is implied due to the shortened C6–C18 bond length of 1.34 Å compared to approximately 1.5 Å for the other C–Me lengths. This is bent away from the metal, creating an angle of 35.0° between the best planes of the five metal bound carbons (C3, C4, C5, C6, C8) and the plane of the

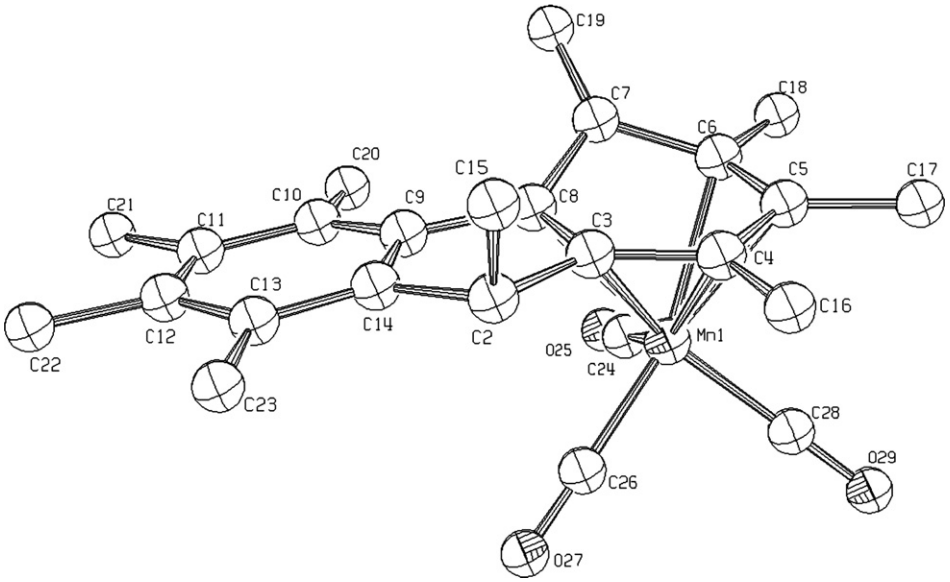


Fig. 4a. Structure of **2**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 50%.

double bond and its neighbouring carbons (C6, C7, C8, C19). This represents the first example of fluorene coordinating to a metal in this way. Details of the crystal are given in Table 1, and relevant bond lengths and angles are given in Table 2.

The reason for this unusual deprotonation may be ascribed to the presence of a methyl group at the 9-position of the ligand. The inductive effects of this group act to destabilise the anion that would form in this position if deprotonation were to occur. This leads to deprotonation of a ring substituent, as the negative charge generated may be delocalised over the atoms bound to the metal. The reason that the methyl group at the rear of the molecule is selectively deprotonated is due to steric effects. In all Flu* complexes that have been crystallographically characterised, including the free ligand, the two methyl groups in the "bay" area of the molecule are significantly bent out of plane of the rest of the arene fragment, shown in Fig. 5 [16,18].

Table 1
Crystallographic data and details of the refinement of **2**

| | |
|---|---|
| Crystal size (mm) | $0.08 \times 0.08 \times 0.24$ |
| Description of crystal | Yellow prism |
| Chemical formula | $C_{28}H_{30}MnO_3$ |
| Formula weight | 469.47 |
| Temperature (K) | 150 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 8.1398(4) |
| $b$ (Å) | 8.9020(4) |
| $c$ (Å) | 18.2830(9) |
| $\alpha$ (°) | 91.9230(19) |
| $\beta$ (°) | 96.275(2) |
| $\gamma$ (°) | 117.099(3) |
| Cell volume (Å$^3$) | 1167.09(10) |
| $Z$ | 2 |
| Calculated density (Mg/m$^3$) | 1.336 |
| Absorption coefficient (mm$^{-1}$) | 0.593 |
| $F_{000}$ | 494 |
| Absorption correction | Semi-empirical from equivalent reflections |
| Transmission coefficients (minimum and maximum) | 0.87, 0.95 |
| $\theta$ Range for data collection (°) | $5.0 \leqslant \theta \leqslant 27.5$ |
| Index ranges | $-10 \leqslant h \leqslant 10, -11 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 23$ |
| Reflections measured | 13126 |
| Unique reflections | 5106 |
| $R_{int}$ | 0.045 |
| Observed reflections ($I > 3\sigma(I)$) | 3738 |
| Refinement method | Full-matrix least-squares on $F$ |
| Parameters refined | 366 |
| Weighting scheme | Chebychev 3-term polynomial |
| Goodness of fit | 1.0916 |
| $R$ | 0.0399 |
| $wR$ | 0.0456 |
| Residual electron density (minimum and maximum) (e Å$^{-3}$) | −0.49, 0.27 |

Table 2
Relevant bond lengths and angles for **2**

| | |
|---|---|
| *Lengths (Å)* | |
| Mn–C3 | 2.165(2) |
| Mn–C4 | 2.148(2) |
| Mn–C5 | 2.159(2) |
| Mn–C6 | 2.239(2) |
| Mn–C8 | 2.238(2) |
| Mn–C3,C4,C5,C6,C8 centroid | 1.70 |
| C3–C4 | 1.420(3) |
| C4–C5 | 1.441(3) |
| C5–C6 | 1.413(3) |
| C6–C7 | 1.489(3) |
| C7–C8 | 1.470(3) |
| C8–C3 | 1.418(3) |
| C4–C16 | 1.504(3) |
| C5–C17 | 1.510(3) |
| C6–C18 | 1.507(3) |
| C7–C19 | 1.336(3) |
| *Angles (°)* | |
| C3,C4,C5,C6,C8 and C6,C7,C8,C19 planes | 35.0 |
| C3,C4,C5,C6,C8 and other $C_6$ plane | 7.8 |
| C6–C7–C8 | 108.11(18) |

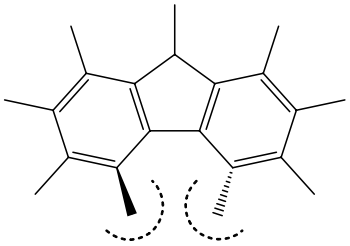

Fig. 5. Steric clash between methyl groups in the bay area of Flu*H causing the methyl groups to bend out of plane, and the whole molecule to be bent.

This steric clash between these two substituents leads to the large bend that is seen in Flu* containing complexes. As may be seen in Fig. 4, the removal of a proton from one of these methyl groups and the subsequent formation of the double bond relieves this strain in the molecule. The bend angle of 35° is slightly larger than the corresponding angle in the deprotonated $(C_6Me_6)Mn(CO)_3$, [19] indicating the relief of steric strain. The remainder of the Flu*H skeleton is almost planar, with an angle of 7.8° between the best planes of the coordinated and uncoordinated arene rings. This angle is significantly lower than that reported for other Flu* complexes, and appears to be due to the relief of steric strain by deprotonation.

## 4. Conclusion

$[(\eta^6\text{-Flu*H})Mn(CO)_3]PF_6$ (**1**) has been synthesised via well established methods. IR analysis of this complex indicates that the Flu*H ligand acts as a strong electron donor, as in other similar complexes. The reaction of **1** with

$^t$BuOK does not lead to the expected deprotonation of the ligand at the 9-position, but instead a methyl group at the rear of the molecule is deprotonated. Complex **2** has been structurally characterised, and shows a previously unknown coordination mode of fluorene. This unexpected deprotonation may be explained on both steric and electronic grounds.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 628336 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.025.

## References

[1] J.H. Rigby, M.A. Kondratenko, Top. Organometall. Chem. 7 (2004) 181.
[2] F. Rose-Munch, E. Rose, Eur. J. Inorg. Chem. (2002) 1269.
[3] M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Publisher Pergamon Press, Oxford, 1995 (Chapters 9.1, 9.2).
[4] S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Publisher Pergamon Press, Oxford, 1995 (Chapter 9.3).
[5] M. Oh, J.A. Reingold, G.B. Carpenter, D.A. Sweigart, Coord. Chem. Rev. 248 (2004) 561.
[6] S. Sun, C.A. Dullaghan, D.A. Sweigart, J. Chem. Soc., Dalton Trans. (1996) 4493.
[7] J.W. Johnson, P.M. Treichel, J. Chem. Soc., Chem. Commun. (1976) 688.
[8] L.F. Veiros, J. Organomet. Chem. 587 (1999) 221.
[9] M.E. Rerek, F. Basolo, Organometallics 3 (1984) 647.
[10] M.G. Yezernitskaya, B.V. Lokshin, V.I. Zdanovich, I.A. Lobanova, N.E. Kolobova, J. Organomet. Chem. 234 (1982) 329.
[11] P.M. Treichel, K.P. Fivizzani, K.J. Haller, Organometallics 1 (1982) 931.
[12] P.M. Treichel, J.W. Johnson, Inorg. Chem. 16 (1977) 749.
[13] P.W. Betteridge, J.R. Cooper, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Cryst. 36 (2004) 1487.
[14] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[15] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
[16] J. Moss, J. Thomas, A. Ashley, A.R. Cowley, D. O'Hare, Organometallics 25 (2006) 4279.
[17] J.A. Reingold, K.L. Virkaitis, G.B. Carpenter, S. Sun, D.A. Sweigart, P.T. Czech, K.R. Overly, J. Am. Chem. Soc. 127 (2005) 11146.
[18] P. Bazinet, K.A. Tupper, T.D. Tilley, Organometallics 25 (2006) 4286.
[19] D.M. LaBrush, D.P. Eyman, N.C. Baenziger, L.M. Mallis, Organometallics 10 (1991) 1026.