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Synthesis and X-ray Crystal Structure of $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$: An Example of the Rare $M-X-Tl^{I}$ Linkage (X = Halide)

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Summary: Reaction of solid TlCl with $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ in CH_2Cl_2 solvent yields the dimeric complex $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$ in 80% isolated yield. The C_5H_5 and C_5Me_5 analogues do not react with TlCl, suggesting a steric basis for the reaction of the C_5Ph_5 material.

Introduction

Reaction of thallium(I) ion with organometallic complexes often results in abstraction of halide ions, forming organometallic cations and insoluble TlX salts.[1] However, on rare occasions thallium(I) actually coordinates to metal-bound halide ions to form soluble coordination compounds, rather than removing the halide.[2] In no case was the formation of these thallium complexes reported as the result of a targeted synthesis. The known examples of such organometallic coordination compounds include $(COD)_2Rh(\mu\text{-}Cl)TlPt_3(CO)_3(PCy_3)$,[3] $[([9]aneS_3)(PPh_3)Ru(\mu\text{-}Cl)_2Tl]_2$,[4] $[(P(CH_2C_2PPh_2)_3)RuH(\mu\text{-}Cl)Tl]_2{}^{2+}$,[5] $[(Tl(18\text{-}crown\text{-}6)_4MCl_4][TlCl_4]_2$ (M = Cu, Zn),[6] $[(dppe)_2Ru(\mu\text{-}F)_2Tl]PF_6$ (dppe = $Ph_2CH_2CH_2PPh_2$),[7] $Tl(\mu\text{-}F)_3Ru(PPh_3)_3$,[8] $((Ph_3P)_2Ru)(\mu\text{-}Cl)(\mu_3\text{-}F)(\mu_3\text{-}Cl)_2Tl$,[8] $[Tp'YCl(\mu\text{-}Cl)_2Tl]_2$ (Tp′ = HB(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)$_2$),[9] $[\{Ru(C\equiv C^tBu)(Cy_2P(CH_2)_4PCy_2)(\mu\text{-}Cl)_3]Tl$,[10] $[Ru(MeO(CH_2)_3PCH_2CH_2P(CH_2)_3OMe)_2(\mu\text{-}Cl)_2Tl]_x$,[11] and $[(P2)M(\mu\text{-}Cl)_2Tl_2(\mu\text{-}Cl)_2(P2)](OTf)_2$ (M = Pd, Pt; P2 = Ph_2P(tetrathiafulvalene)).[12]

These complexes share the common structural feature of an $M-X-Tl^{I}$ linkage. All but one include late transition metals or main group metals as the second metal in the bridge. Likewise, 12 of the 13 transition metals lie in the +1 or +2 oxidation state, with yttrium as the only exception.[9] Beyond these features, the complexes seem to bear little else in common. They include both hard and soft ancillary ligands, have thallium ions that reside in protected and exposed environments, exist as both monomeric and cluster compounds, and include metals from all three transition series, although a preference appears to exist for second-row transition metals.

The scarcity of these complexes relative to the number of reactions that could produce them suggests they possess limited stability. Consistent with this hypothesis, several of the papers report that the complexes extrude TlX under mild conditions or very similar complexes do not coordinate thallium(I). For example, Schröder and Yellowlees found that $[([9]aneS_3)(PPh_3)Ru(\mu\text{-}Cl)_2Tl]_2$ is stable in dichloromethane solution, but converts to $[([9]aneS_3)(PPh_3)Ru(\mu\text{-}Cl)]_2$ in either acetone or nitromethane with concomitant loss of TlCl.[4] Likewise, Bianchini reports that warming a solution of $[(P(CH_2C_2PPh_2)_3)RuH(\mu\text{-}Cl)Tl]_2{}^{2+}$ in tetrahydrofuran to reflux causes loss of TlCl to form the $(P(CH_2C_2PPh_2)_3)RuH^+$ cation.[5] In a different vein, Barthazy and co-workers observed that when $Ph_2P(CH_2)_3PPh_2$ replaces $Ph_2P(CH_2)_2PPh_2$ in the starting $(dppe)_2RuCl^+$ complex, no thallium adduct forms on reaction with TlF.[7]

As for the complexes just described, the thallium(I)-bridged complex described in this report was first prepared by serendipity. An electrospray mass spectrum of $[(C_5Ph_5)Cr(\mu\text{-}Cl)Cl]_2$ displays no parent ion peak, but rather exhibits a high mass peak consistent with $[(C_5Ph_5)_2Cr_2Cl_3]^+$.[13] It seemed possible that this might occur by loss of a terminal chloride ligand followed by a structural rearrangement to $[(C_5Ph_5)Cr(\mu\text{-}Cl)_3Cr(C_5Ph_5)]^+$.[14] Herein, we report the rational synthesis and characterization of the unusual complex $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$, which initially

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(1) (a) Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528−533. (b) Filippou, A. C.; Grünleiter, W. *J. Organomet. Chem.* **1989**, *378*, 387−399. (c) Antiñolo, A.; Carrillo, F.; Chaudret, B.; Fajardo, M.; García-Yuste, S.; Lahoz, F. J.; Lanfranchi, M.; López, J. A.; Otero, A.; Pellinghelli, M. A. *Organometallics* **1995**, *14*, 1297−1301. (d) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2002**, *41*, 147−151.

(2) Two other types of compounds containing this linkage exist, but are also rare: (a) organothallium compounds bridging to a main group halide (e.g., $(mes)_6Tl_4(\mu\text{-}Br)_{10}(\mu_3\text{-}Br)_4[Ga_2(GaBr)_2]$: Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414−415) and (b) inorganic coordination complexes (e.g., Tl_2PdCl_4: Schüpp, B.; Keller, H.-L. *Z. Anorg. Allg. Chem.* **1999**, *625*, 379−381).

(3) Ezomo, O. J.; Mingos, D. M. P.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987**, 924−925.

(4) Blake, A. J.; Christie, R. M.; Roberts, Y. V.; Sullivan, M. J.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1992**, 848−849.

(5) Bianchini, C.; Masi, D.; Linn, K.; Mealli, C.; Peruzzini, M.; Zanobini, F. *Inorg. Chem.* **1992**, *31*, 4036−4037.

(6) Kahwa, I. A.; Miller, D.; Mitchel, M.; Fronczek, F. R.; Goodrich, R. G.; Williams, D. J.; O'Mahoney, C. A.; Slawin, A. M.; Ley, S. V.; Groombridge, C. J. *Inorg. Chem.* **1992**, *31*, 3963−3970.

(7) Barthazy, P.; Togni, A.; Mezzetti, A. *Organometallics* **2002**, *21*, 3472.

(8) Becker, C.; Kieltsch, I.; Broggini, D.; Mezzetti, A. *Inorg. Chem.* **2003**, *42*, 8417−8429.

(9) Kunrath, F. A.; Casagrande, O. L., Jr.; Toupet, L.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 4803−4806.

(10) Drouin, S. D.; Foucault, H. M.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2004**, *23*, 2583−2590.

(11) Szymczak, N. K.; Han, F.; Tyler, D. R. *Dalton Trans.* **2004**, 3941−3942.

(12) Devic, T.; Batail, P.; Fourmigué, M.; Avarvari, N. *Inorg. Chem.* **2004**, *43*, 3136−3141.

(13) Price, W.D.; Castellani, M. P. Unpublished results.

(14) At the beginning of this project, such trihalobridged species were unknown for cyclopentadienyl-chromium complexes. Several months after having attempted the chemistry described in this paper, Wei and Stephan reported the synthesis and X-ray crystal structure of $(C_5Me_5)Cr(\mu\text{-}Cl)_3Cr(C_5Me_5)^+$ by removing a terminal halide from $[(C_5Me_5)CrCl(\mu\text{-}Cl)]_2$ using $AlCl_3$. Wei, P.; Stephan, D. W. *Organometallics* **2003**, *22*, 1712−1717.

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Table 1. Crystal and Refinement Data for $[(C_5Ph_5)Cr(\mu\text{-}Cl)_2ClTl]_2 \cdot 2CH_2Cl_2$

formula	$C_{72}H_{54}Cl_{10}Cr_2Tl_2$
fw	1786.50
cryst syst	monoclinic
space group	$P2(1)/n$
a, Å	12.519(3)
b, Å	17.679(4)
c, Å	15.887(3)
α, deg	90
β, deg	110.865(4)
γ, deg	90
V, Å^3	3285.7(12)
Z	4
D(calcd), g/cm^3	1.806
abs coeff, mm^{-1}	5.661
diffractometer	Bruker/P4 (APEX CCD)
radiation	Mo Kα (λ = 0.710 73 Å)
temp, K	218(2)
final R indices ($[I > 2\sigma(I)]$), %	R = 3.61, wR = 8.31
R indices (all data), %	R = 4.96, wR = 8.87

resulted from an attempt to prepare that trichloro-bridged species by a halide abstraction reaction with $TlPF_6$.

Experimental Section

General Data. All reactions of air- and moisture-sensitive materials were performed under a nitrogen atmosphere employing standard Schlenk techniques unless otherwise stated. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train. Dichloromethane (Acros) was distilled from CaH_2 under nitrogen. Hexane was deoxygenated prior to use by bubbling nitrogen through it for 30 min. $[(C_5R_5)CrCl(\mu\text{-}Cl)]_2$ (R = H,[15] Me,[16] Ph[17]) were prepared according to literature procedures. Thallium(I) chloride (Alfa) was used as received without further purification. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

X-ray Structural Determination. Crystallographic data for $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2 \cdot 2CH_2Cl_2$ are collected in Table 1. The space group was determined from systematic absences and the structure solved using heavy-atom methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in idealized locations. All software was contained in the Bruker SMART, SAINT, and SHELXTL libraries.

Preparation of $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2 \cdot 2CH_2Cl_2$ ($1 \cdot 2CH_2Cl_2$). Dichloromethane (15 mL) was added to a flask containing $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ (0.050 g, 0.044 mmol) and TlCl (0.032 g, 0.13 mmol). Following a gentle overnight reflux, the solution turned emerald green with a small amount of the white TlCl solid still present. The mixture was filtered via cannula into a Schlenk tube and layered with hexane (10 mL). The layers combined to yield $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2 \cdot 2CH_2Cl_2$ as a green powder (0.063 g, 80%). Mp range: 246−248 °C (dec). Anal. Calcd for $C_{72}H_{54}Cl_{10}Cr_2Tl_2$: C, 48.41; H, 3.05. Found: C, 48.53; H, 2.95.

Results and Discussion

Synthesis. Reaction of the $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ dimer with TlCl yielded the dark olive green complex $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$ (**1**) in 80% yield (eq 1).

$$[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2 + 2\ TlCl \rightarrow 2\ [(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2 \quad (1)$$

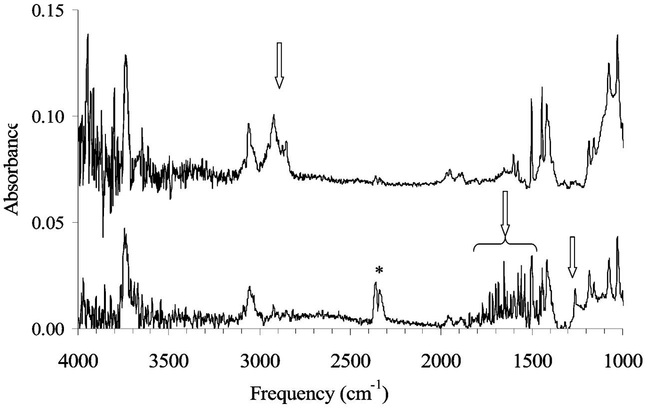

Figure 1. Infrared spectra of $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$ (bottom) and $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ (top). Arrows indicate locations of significant peaks that differ between the spectra. The fine structure beneath the bracket is real. The asterisk denotes CO_2.

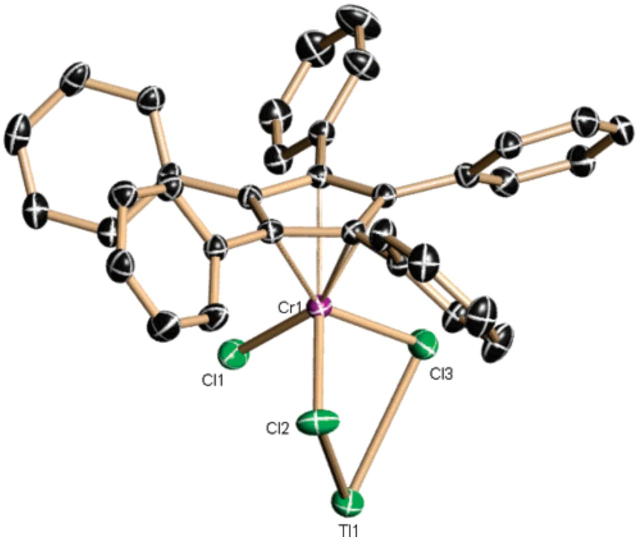

Figure 2. Molecular structure and labeling scheme for $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2 \cdot 2CH_2Cl_2$ (**1**). Thermal ellipsoids are shown at 40% probability.

The starting chromium dimer and thallium-containing product are nearly identical in color. While $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ possesses extremely low solubility in noncoordinating solvents,[17] **1** dissolves readily in dichloromethane. Thus, the reaction changes from an initial mixture of green and white solids in a nearly colorless solution to a dark green solution with excess solid TlCl present as the reaction progresses. Complex **1** also forms in much lower yields from the reaction between $TlPF_6$ and $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$. This reaction also produces a significant amount of excess TlCl that precipitates from solution.

The generality of this synthetic approach was examined by repeating reaction 1 with $[(C_5R_5)Cr(\mu\text{-}Cl)Cl]_2$ (R = H (Cp), Me (Cp*)) in place of $[(C_5Ph_5)Cr(\mu\text{-}Cl)Cl]_2$. In both cases, no analogous reaction occurs and the starting chromium dimers were recovered unchanged (verified by their elemental analyses,[18] decomposition temperatures, and infrared spectra). In contrast, the infrared spectra of **1** and $[(C_5Ph_5)Cr(\mu\text{-}Cl)Cl]_2$ differ in significant ways (Figure 1).

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(15) Köhler, F. H.; de Cao, R.; Ackermann, K.; Sedlmair, J. *Z. Naturforsch.* **1983**, *38b*, 1406−1411.

(16) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570−2577.

(17) Hutton, M. A.; Durham, J. C.; Grady, R. W.; Harris, B. E.; Jarrell, C. S.; Mooney, J. M.; Castellani, M. P.; Rheingold, A. L.; Kölle, U.; Korte, B. J.; Sommer, R. D.; Yee, G. T. Yee; Boggess, J. M.; Czernuszewicz, R. S. *Organometallics* **2001**, *20*, 734−740.

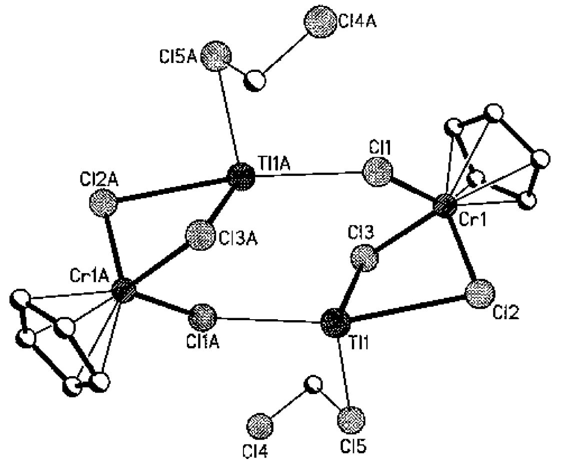

Figure 3. Inversionally symmetrical intermolecular association via long Tl−Cl linkages with further coordination of a molecule of CH_2Cl_2 to Tl. Phenyl groups and hydrogen atoms have been deleted for clarity.

$[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$ seems most similar to the only other thallium-containing early transition metal complex $[Tp'YCl(\mu\text{-}Cl)_2Tl]_2$.[9] Both contain metals in relatively high oxidation states. The yttrium complex has all hard ligands, while the chromium complex has chloride ligands and an electron-poor C_5Ph_5 ligand.[19]

To date, only about a dozen organotransition metal complexes containing the $M-X-Tl^I$ (M = transition metal ion, X = halide ion) linkage have been reported (*vide supra*). As suggested earlier, their rarity may arise because these complexes possess marginal stability. In particular, they may tend to form only when their parent organometallic molecule is not itself highly stable. Consistent with this hypothesis, $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2$ forms while the analogous Cp and Cp* complexes do not. An examination of the structures of the starting chromium dimers suggests a reason for this reactivity pattern. Structurally uncongested $[CpCr(\mu\text{-}Cl)Cl]_2$ possesses a Cl(bridging)−Cr−Cl(terminal) angle of ca. 96°,[20] while the angle in the more crowded $[Cp^*Cr(\mu\text{-}Cl)Cl]_2$ is ca. 97°.[21] In contrast, the angle decreases significantly to ca. 92° in the highly crowded molecule $[(C_5Ph_5)Cr(\mu\text{-}Cl)Cl]_2$.[17] All other angles in the three chromium dimers are similar. This apparently puts sufficient strain on the $Cr_2(\mu\text{-}Cl)_2$ dimer core in $[(C_5Ph_5)Cr(\mu\text{-}Cl)Cl]_2$ to make it susceptible to ligation and cleavage by TlCl. It is interesting that the effect is not to make removal of a chloride ion easier.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2\cdot 2CH_2Cl_2$

Distances	
Cr−C(1)	2.301 (3)
Cr−C(2)	2.267 (3)
Cr−C(3)	2.279 (3)
Cr−C(4)	2.276 (3)
Cr−C(5)	2.263 (3)
Cr−CNT[a]	1.925(3)
Cr−Cl(1)	2.3153 (11)
Cr−Cl(2)	2.3099 (12)
Cr−Cl(3)	2.3242 (12)
Tl(1)−Cl(2)	3.0556 (11)
Tl(1)−Cl(3)	3.0260 (11)
Tl(1)−Cl(1a)	3.566(1)
Tl(1)−Cl(5)	3.445(1)
Angles	
CNT−Cr−Cl(1)	126.8(1)
CNT−Cr−Cl(2)	124.0(1)
CNT−Cr−Cl(3)	121.8(1)
Cl(1)−Cr−Cl(2)	91.60 (5)
Cl(1)−Cr−Cl(3)	89.90 (4)
Cl(2)−Cr−Cl(3)	92.94 (5)
Cr−Cl(2)−Tl(1)	87.15 (4)
Cr−Cl(3)−Tl(1)	87.61 (4)
Cl(2)−Tl(1)−Cl(3)	67.07 (3)
Cr(1)−Cl(1)−Tl(1a)	97.02(4)
Cl(2)−Tl(1)−Cl(5)	87.10(3)
Cl(2)−Tl(1)−Cl(1a)	137.29(3)

[a] Centroid.

Molecular Structure of $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2\cdot 2CH_2Cl_2$. The X-ray crystal structure of $[(C_5Ph_5)CrCl(\mu\text{-}Cl)_2Tl]_2\cdot 2CH_2Cl_2$ is displayed in Figures 2 and 3. Bond distances and angles are listed in Table 2. The chromium resides in a slightly distorted octahedral environment. Bond distances and angles resemble those in the parent $[(C_5Ph_5)CrCl(\mu\text{-}Cl)]_2$ molecule. Bond lengths are unexceptional, with the Tl−Cl bonds lying near the middle of the range of lengths reported in known bridging complexes. The Cl−Tl−Cl bond angle, 67.1°, is similar to that found for both the terminal complex $[\{Ru(C\equiv C^tBu)(Cy_2P(CH_2)_4PCy_2)(\mu\text{-}Cl)_3]Tl$ (69.4°)[10] and bridging complex $[([9]aneS_3)(PPh_3)Ru(\mu\text{-}Cl)_2Tl]_2$ (67.6°)[4] but significantly different from several of the other complexes.[9,11,12] The molecule exists as a weakly bound dimer in the solid state. Thus, each thallium ion lies more than 0.5 Å closer to its nearest chloride neighbors than to the distal chloride in the other half of the dimer. The thallium also binds weakly to the dichloromethane solvate; with a similar distance separating it from the chlorine on CH_2Cl_2.

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Supporting Information Available: Crystal data, in CIF format, is available free of charge via the Internet at http://pubs.acs.org.

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(18) Elemental analyses of the recovered solids include small amounts of thallium (0.50% for R = H, and 1.50% for R = Me), but this probably results from trace contamination of the starting dimers by TlCl. If one assumes that the thallium actually results from $[(C_5R_5)CrCl(\mu\text{-}Cl)_2Tl]_2\cdot 2CH_2Cl_2$ (R = H, Me), it would be very difficult to detect the compounds using any of the methods described in this paper. If the samples contained only $[(C_5R_5)CrCl(\mu\text{-}Cl)_2Tl]_2\cdot 2CH_2Cl_2$ and the starting chromium dimer, then the material recovered for R = H would contain less than 4% of the thallium complex, while R = Me would contain less than 1.5% thallium complex.

(19) Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116−123.

(20) Köhler, F. H.; de Cao, R.; Ackermann, K.; Sedlmair, J. *Z. Naturforsch.* **1983**, *38B*, 1406−1411.

(21) Köhler, F. H.; Lachmann, J.; Müller, G.; Zeh, H.; Brunner, H.; Pfauntsch, J.; Wachter, J. *J. Organomet. Chem.* **1989**, *365*, C15−C18.