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Novel Heterobimetallic Coordination of the $H_2B(mt)_2$ Ligand: The Complex $[Mo(SnMe_2Cl)(CO)_3\{\mu\text{-}S{:}\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ (mt = methimazolyl)

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Summary: Molybdenum stannyl complexes ligated by poly(methimazolyl)borate ligands are accessible via complementary strategies involving oxidative addition of either $Ph_3Sn\{HB(mt)_3\}$ (mt = methimazolyl) or $[Me_2Sn\{H_2B(mt)_2\}]Cl$ to molybdenum(0) precursors or alternatively via reactions of halostannanes with the salts $Na[Mo(CO)_3\{H_xB(mt)_{4-x}\}]$ (x = 1, 2). One example provides a novel complex in which the $H_2B(mt)_2$ ligand bridges both molybdenum and tin, thereby providing a model for an intermediate in the oxidative addition protocol.

The tris- and bis(methimazolyl)borate ligands introduced respectively by Reglinski[1] and Parkin[2] have been quickly embraced by coordination chemists, in particular those concerned with bioinorganic chemistry. One attractive feature is the perception that they would serve as "tame thiolates"[3] for the purposes of modeling sulfur donor groups in metalloenzymes, with a reduced propensity for oligomerization via sulfur bridging. Our interest in these ligands focuses rather on their use as supports for organometallic complexes, presuming that they will offer ligative properties intermediate between Trofimenko's anionic poly(pyrazolyl)borates[4] and neutral 1,4,7-trithiacyclononane.[5] This has led us to a range of organometallic derivatives of the $H_2B(mt)_2$[6] and $HB(mt)_3$[6−8] ligands in support of such an analogy. More notable however has been the departure from analogy that arises for later transition metals with high d-occupancies, whereby access is afforded to a novel range of cage complexes (metallaboratranes) via activation of the borohydride group.[8] In furthering our studies, we have now turned our attention to the development of stannyl derivatives of the poly(methimazolyl)borate ligands as potential transfer reagents. This has so far met with somewhat dubious success in attempts to deploy $Ph_3Sn\{HB(mt)_3\}$ for the synthesis of derivatives of the group 5 metals. Rather than simple halide metathesis with $[MCl_4(\eta\text{-}C_5H_5)]$ (M = Nb, Ta), novel complexes of the new chlorobis(methimazolyl) borate ligand were obtained.[9] Herein we wish to report that stannyl reagents are indeed effective for the introduction of $H_2B(mt)_2$ or $HB(mt)_3$ ligands into the coordination sphere of low-valent group 6 metals.

Treating a solution of either $[Mo(NCMe)_3(CO)_3]$ or more conveniently $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ with $Ph_3Sn\{HB(mt)_3\}$ leads to the smooth formation of the new complex $[Mo(SnPh_3)(CO)_3\{HB(mt)_3\}]$ (**1a**).[10a] The identical complex and its tungsten analogue (**1b**) may be obtained from the reaction of $Na[M(CO)_3\{HB(mt)_3\}]$ (M = Mo, W)[6a] with chlorotriphenylstannane. Spectroscopic data support the gross formulation; however they do not unequivocally distinguish between two possibilities as far as the arrangement of ligands. The NMR data indicate a highly symmetrical complex with only one phenyl, one carbonyl, and one methimazolyl environment. This would be consistent with either a (tin) capped octahedral geometry or alternatively a complex that is fluxional on the NMR time scales (e.g., "mt"-dissociation[7]). However, the intensity profile for the two ν(CO) infrared absorptions [1969(45), 1876(135) cm^{-1}] is suggestive of a symmetric obtuse C_{3v}-$M(CO)_3$ arrangement. Such a geometry has been established in the solid state for the related complexes $[Mo(SnPh_3)(CO)_3(L)]$ [L = $HB(pz)_3$, $HB(pzMe_2\text{-}3,5)_3$].[11]

Attempts to widen the approach to other stannyl derivatives met with various success, depending on the efficacy of the synthesis of the appropriate tin reagent. We will report elsewhere in detail on the extensive structural chemistry of organotin derivatives of $H_xB(mt)_{4-x}$ ligands; however the compound derived from the reaction of $Na[H_2B(mt)_2]$ and Me_2SnCl_2 is particularly noteworthy. In contrast to the crystallograhically char-

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[1] Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.

[2] Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680.

[3] Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 4022.

[4] Tofimenko, S. *Scorpionates: The Coordination Chemistry of Poly(pyrazolyl)borate Ligands*; Imperial College Press: London, 1999.

[5] Blake, A. J.; Schroder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.

[6] (a) Foreman, M. R. St-J.; Hill, A. F.; Tshabang, N.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 5593. (b) Abernethy, R. J.; Hill, A. F.; Neumann, H.; Willis, A. C. *Inorg. Chim. Acta* **2005**, *358*, 1605.

[7] Foreman, M. R. St-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3831.

[8] (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759. (b) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446. (c) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913. (d) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656. (e) Crossley, I. R.; Foreman, M. R. St-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221. (f) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (g) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 4889.

[9] Hill, A. F.; Smith, M. K. *Chem. Commun.* **2005**, 1920.

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acterized molecular compound $Ph_3Sn\{HB(mt)_3\}$,[9] the product is the “salt” $[Me_2Sn(mt)_2BH_2]Cl$ (**2·Cl**), which we have structurally characterized (Figure 1).[10b] The geometry of the cation is reminiscent of that observed for the recently reported heterocyclic salt $[H_2C(mt)_2BH_2]Cl$,[12] in which a $SnMe_2$ group in **2** replaces the methylene bridge in a chair conforming eight-membered heterocycle. However, a secondary structure exists in the solid state arising from two types of interaction. The first involves four weak Sn−Cl associations about an inversion center [Figure 1a, Sn−Cl: 3.00(2) Å, Cl−Sn−Cl: 79.05(1)°, Sn−Cl−Sn: 100.95(1)°], the effect of which is to substantially open the C1−Sn−C2 angle from tetrahedral to 159.8(2)°. The second interaction involves hydrogen bonding between the chloride and imidazolyl protons on two adjacent $\mathbf{2}^+$ units (Cl1···H13: 2.79(2) Å; C13−H13···Cl1: 161.0(2)°, Figure 1b). The entire network is generated by symmetry from half a molecule of **2·Cl**. Presumably, in solution this hydrogen bonding is lost and the chloride associates more strongly with the tin center(s).

Despite the ionic nature of **2·Cl**, it serves as an effective substrate for oxidative addition to $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ and indeed indirectly provides insight as to how such reactions may occur at the molybdenum center. Treating $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ with **2·Cl** provides a compound of gross composition $[Mo(SnClMe_2)(CO)_3\{H_2B(mt)_2\}]$ (**3**).[10c] The same complex may also be obtained from the reaction of the salt $Na[Mo(CO)_3\{H_2B(mt)_2\}]$ with dichlorodimethylstannane. Spectroscopic data however reveal some features of note. First, a broad resonance is observed at δ −4.8 in the ^1H NMR spectrum, in a region typical of three-center two-electron B−H−Mo interactions in $H_2B(mt)_2$ complexes.[6] The infrared spectrum indicates that the molecule has no element of symmetry; however the ^1H NMR spectrum shows that there is only one methimazolyl and one $SnCH_3$ environment on the NMR time scale. The complex was therefore characterized crystallographically. The results of this study are summarized in Figure 2, from which it is clear that the coordination about molybdenum is quite distinct from that in **1**.

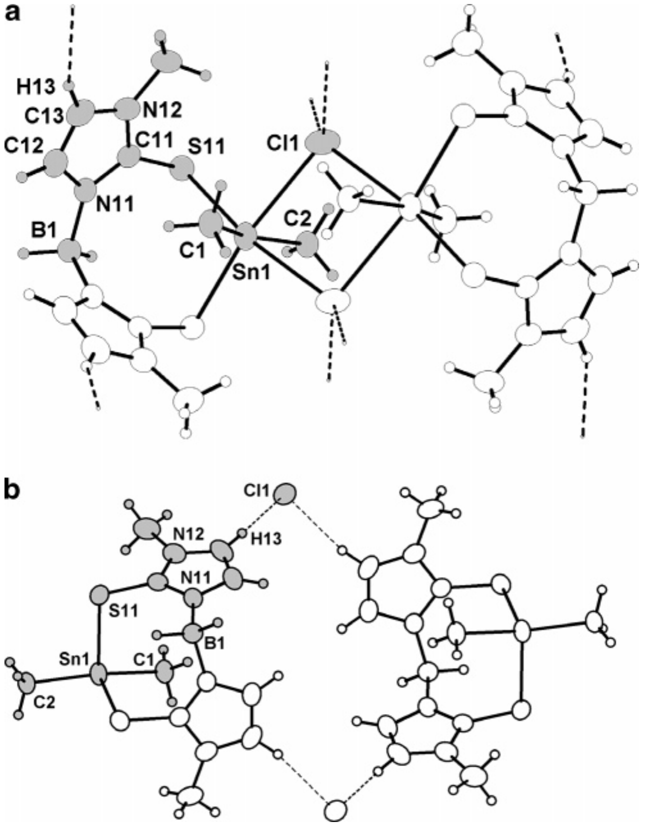

Figure 1. Geometry of **2·Cl** in a crystal (50% displacement ellipsoids, one set of crystallographically unique atoms indicated in gray): (a) $Sn_2(\mu\text{-}Cl)_2$ association; (b) hydrogen bond associaion.

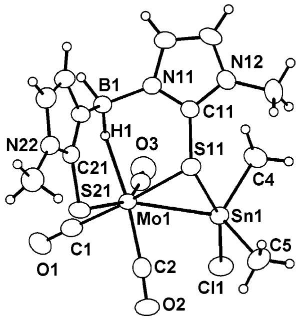

Figure 2. Molecular geometry of **3** (50% displacement ellipsoids).

The complex involves coordination of the *intact* $ClMe_2Sn\{H_2B(mt)_2\}$ ligand through two sulfur donors, one three-center two-electron B−H−Mo interaction and a

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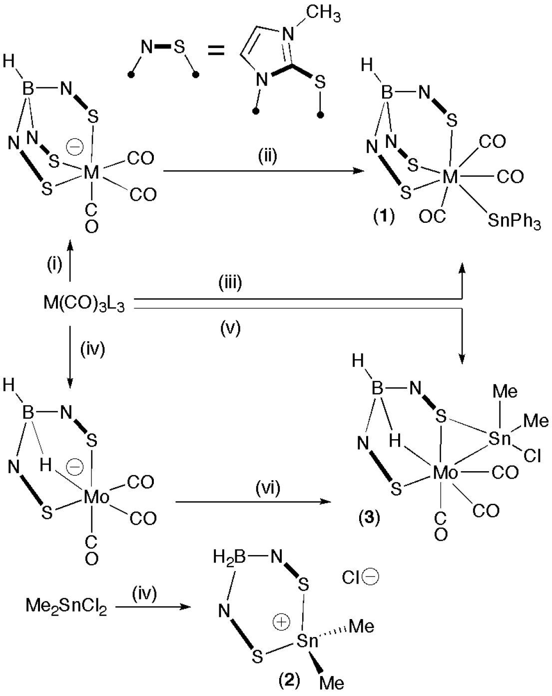
(10) (a) **1a**: A mixture of $[Sn\{HB(mt)_3\}Ph_3]$ (0.25 g, 0.36 mmol)[9] and $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ (0.10 g, 0.36 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 h, during which time the color changed from a red solution to yellow. The resulting solution was filtered and concentrated. Ethanol (20 mL) was then added and the total solvent volume further reduced to provide a yellow solid. The product was recrystallized from CH_2Cl_2 and hexane. Yield = 0.17 g (53%). IR (CH_2Cl_2): 1969, 1876 (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 3.55 (s, 9 H, NMe), 6.80 (s, 6 H, NCH=CH), 7.27, 7.65, 7.67 (m × 3, 15 H, SnC_6H_5). $^{13}C\{^1H\}$: δ_C 223.8 (MoCO), 158.9 (C=S), 137.2, 127.9 [$C^{2,3,5,6}(C_6H_5)$], 136.2 [$C^4(C_6H_5)$], 129.2 [$C^1(C_6H_5)$], 123.1, 120.2 (NCHCHN), 34.76 (CH_3). ^{11}B: δ_B −2.43. FAB-MS: 885 $[HM]^+$. Anal. Found: C, 45.00; H, 3.67; N, 9.54. Calcd for $C_{33}H_{31}BMoN_6O_3S_3Sn$: C, 44.98; H, 3.55; N, 9.54% (b) **2·Cl**: A mixture of Me_2SnCl_2 (0.42 g, 1.89 mmol) and $Na[H_2B(mt)_2]$ (0.48 g, 1.90 mmol) in dichloromethane (40 mL) was stirred for 15 h and then filtered to remove NaCl. Addition of hexane (20 mL) followed by slow concentration under reduced pressure afforded white crystals of **2·Cl**. NMR ($CDCl_3$, 25 °C) ^1H: δ 1.024 (s, 6 H, $SnCH_3$), 3.604 (s, 6 H, NMe), 6.854, 6.847 (s × 2, 4 H, NCH=CH). $^{13}C\{^1H\}$: δ_C 150.1 (C=S), 125.3, 121.0 (NCHCHN), 35.56 (NCH_3), 25.82, 13.44 ($SnCH_3$). Crystal data for **2**: $C_{11}H_{18}BClN_4S_2Sn$, $M = 235.4$, monoclinic, $C2/m$ (no. 12), $a = 13.690(3)$ Å, $b = 13.430(3)$ Å, $c = 9.612(2)$ Å, $\beta = 93.91(3)°$, $V = 1763.1(6)$ Å^3, $Z = 8$, $D_c = 1.909$ g cm^{-3}, $\mu(Mo\ K\alpha) = 21.33$ cm^{-1}, $T = 200(2)$ K, 2121 independent measured reflections, F^2 refinement, $R_1 = 0.039$, $wR_2 = 0.097$, 1849 independent observed absorption-corrected reflections [$I > 2\sigma|I|$), $2\theta_{max} = 55°$], 112 parameters. CCDC 250754. (c) A mixture of $[Sn\{H_2B(mt)_2\}Me_2]Cl$ (0.77 g, 1.83 mmol) and $[Mo(CO)_3(C_7H_8)]$ (0.50 g, 1.83 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 h, during which time the reaction changed from a red solution to yellow, and allowed to stir for a further 12 h. The resulting solution was filtered and the solvent reduced to a minimum. Ethanol (10 mL) was added and the total solvent volume reduced to provide a yellow solid. The solid was filtered, washed with hexane (20 mL), followed by diethyl ether (2 × 10 mL), and then dried. The product was recrystallized from CH_2Cl_2 and hexane. Yield = 0.63 g (57%). Data for **3**: IR (CH_2Cl_2) 2457 (ν_{BH}), 2225 (ν_{BHMo}), 2001, 1919, 1889 (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ −4.8 (BHMo), 0.89 [s, 6 H, $SnCH_3$, $^2J(SnH) = 111$ Hz) 3.59 (s, 6 H, NMe), 6.82, 6.84 (s × 2, 4 H, NCH=CH). Anal. Found: C, 29.7; 3.59; N, 11.06. Calcd for $C_{13}H_{18}BClMoN_4O_3S_2Sn·EtOH$: C, 29.97; H, 3.71; N, 11.04. Crystal data for **3**: $C_{13}H_{18}BClMoN_4O_3S_2Sn$, $M = 603.3$, monoclinic, $P2_1/n$ (no. 14), $a = 9.6600(19)$ Å, $b = 21.430(4)$ Å, $c = 10.210(2)$ Å, $\beta = 96.60(3)°$, $V = 2099.6(7)$ Å^3, $Z = 4$, $D_c = 1.774$ Mg m^{-3}, $\mu(Mo\ K\alpha) = 1.986$ mm^{-1}, $T = 200(2)$ K, 4796 independent measured reflections, F^2 refinement, $R_1 = 0.042$, $wR_2 = 0.092$, 4796 independent observed absorption-corrected reflections [$I > 2\sigma(I)$, $2\theta_{max} = 55°$], 245 parameters. CCDC 250755.

(11) Liu, Y.-Y.; Mar, A.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem*. **1988**, *66*, 1997.

(12) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Smith, M. K.; Tshabang, N.; Willis, A. C. *Chem. Commun.* **2004**, 1878.

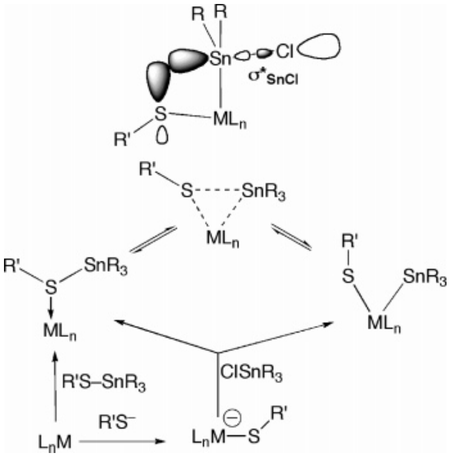
Scheme 1. Synthesis of Stannyl Complexes[a]



[a] L_3 = $(NCMe)_3$, η^6-C_7H_8. (i) $Na[HB(mt)_3]$, (ii) $ClSnPh_3$, (iii) $Ph_3Sn\{HB(mt)_3\}$, (iv) $Na[H_2B(mt)_2]$, (v) $[Me_2Sn(mt)_2BH_2]Cl$ (**2**), (vi) Me_2SnCl_2.

molybdenum–tin bond. The hydrogen atom bridging molybdenum and boron was located [Mo1–H1 2.03(5) Å]; however the Mo1–B1 separation of 2.982(7) Å provides a more precise indication of this interaction.[6a] The 'terminal' (S21) and bridging (S11) Mo–S bond lengths of 2.51(2) and 2.631(3) Å, respectively, indicate a stretching of the latter as a result of coordination to Sn1 [S11–Sn1 2.86(5) Å]. The Mo1–Sn1 separation of 2.80(2) Å falls within the albeit large range of values for Sn^{IV} bound to seven-coordinate Mo^{II}.[11,13] The structure adopted by **3** could be considered as a model for an interrupted oxidative addition of the S–Sn bond that is mechanistically implicit in the synthesis of **1a** and related compounds. In this respect it should be noted that there exist a range of Mo^0 adducts of $SnCl_4$ wherein a three-membered Mo–Cl–Sn ring is adopted in the solid state,[13,14] which might also be considered as modeling intermediates along a Sn–Cl oxidative addition trajectory (Scheme 2). Data for such complexes are summarized in Table S1 (Supporting Information) and fall within the ranges 2.474–2.565 (Mo–ClSn) and 2.687–2.756 Å (Mo–Sn), the latter being less than the Mo–Sn separation in **3**. There is a marked elongation (ca. 20%) of the Sn–Cl bond in such complexes (Sn–ClMo: 2.730–2.889 Å) relative to terminal tin chloride bond lengths (Sn–Cl: 2.314–2.432 Å). In the context of Sn–S oxidative addition to molybdenum, the product of the reaction of Cy_3PCS_2 with $[Mo(SnCl_2Ph)(S_2P(OEt)_2\}(CO)_3(NCMe)]$ has been shown to adopt a weak Sn–S interaction between the coordinated phosphoniodithiocarboxylate and stannyl ligands [2.999(2) Å], albeit significantly longer than the Sn–S interaction in **3**.[15] It is not clear why an "intermediate" should be isolable in what might otherwise be expected to be a concerted Sn–S oxidative addition reaction. However the observation that it is observable in the case of **3** but not for **1a** where Sn–S rupure is complete suggests that the electronegative halide substituent plays a role. Noting that this is disposed trans to the Sn–S bond, we surmise that a basic sulfur lone pair might be considered to donate into the Sn–Cl antibonding (σ^*) orbital (the Sn–Cl bond length is comparatively long, 2.446(13) Å, cf. Table S1), thereby affording some stabilization.

Scheme 2. Interrupted Oxidative-Addition/Reductive-Elimination of S–Sn Bonds at a Metal Center; Interligand Electron Donation from Sulfur (lone pair) to Tin (σ^*_{SnCl} antibonding orbital)



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Supporting Information Available: Full details of the crystal structure analyses of **2** (CCDC250754) and **3** (CCDC250755) in CIF format; Table S1 collating relevant structural data[13] for molybdenum stannyl and stannane complexes This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Cambridge Crystallographic Data Centre. "ConQuest 1.6" CSD 5.25 January 2005 Release. See Supporting Information Table S1 for selected examples.

(14) (a) Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1268. (b) Heinze, K.; Jacob, V.; Feige, C. *Eur. J. Inorg. Chem.* **2004**, 2053. (c) Szymanska-Buzar, T.; Glowiak, T.; Czelusniak, I. *Inorg. Chem. Commun.* **2000**, *2*, 103. (d) Szymanska-Buzar, T.; Glowiak, T. *Polyhedron* **1998**, *17*, 3419. (e) Anderson, R. A.; Einstein, F. W. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 966. (f) Szymanska-Buzar, T.; Glowiak, T.; Czelusniak, I. *J. Organomet. Chem.* **2001**, *640*, 72. (g) Chai, J.-F.; Tang, L.-F.; Jia, W.-L.; Wang, Z.-H.; Wang, J.-T.; Leng, X.-B.; Wang, H.-G. *Polyhedron* **2001**, *20*, 3249. (h) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 5354. (i) Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 694. (j) Szymanska-Buzar, T.; Glowiak, T.; Czelusniak, I. *Polyhedron* **2002**, *21*, 2505.

(15) Barrado, G.; Miguel, D.; Pérez-Martinez, J. A.; Riera, V.; García-Granda, S. *J. Organomet. Chem.* **1994**, *466*, 147.