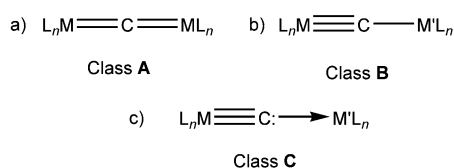


# Homonuclear Carbides

## $[(\mu\text{-C})\{\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$ : A Surprisingly Simple Bimetallic Carbido Complex\*\*

Rowan D. Young, Anthony F. Hill,\* Germán E. Cavigliasso, and Robert Stranger

The bonding in the majority of binuclear  $\mu$ -carbido complexes may, to a first approximation, be described by one of two extreme canonical forms (A and B; Scheme 1). Symmetrical bimetallic complexes in which similar metal centers are bound to the central carbon atom are generally considered to adhere



**Scheme 1.** Classification of binuclear carbido ligands: a) Cumulene (class A), b) metallacarbene (class B), c) polar covalent (class C).

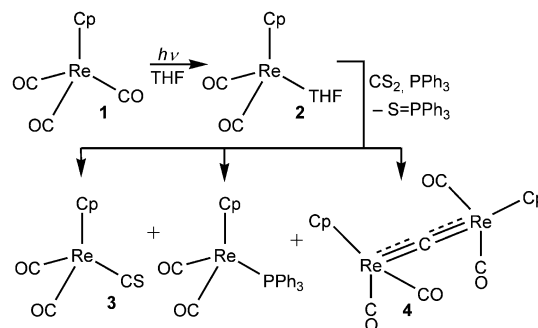
to a dimetallaallene-like bond localization (class A).<sup>[1,2]</sup> Most examples of this type of bonding have so far arisen from the reduction of Group 8 porphyrin complexes in the presence of  $\text{Cl}_4$ ,<sup>[1]</sup> this synthetic strategy ensures that both metal termini are identical, though examples do exist which involve disparate metals.<sup>[3]</sup> The alternative, and more commonly encountered class B “metallacarbene” carbido complex involves essentially localized triple and single metal–carbon bonds that reflect the electronic requirements of the necessarily different metals.<sup>[4]</sup> A third class (C) of bridging carbido ligand has been observed, which might be described as polar covalent or dative in nature; however, at present few examples exist.<sup>[5]</sup>

Despite the attempt above to delineate bonding profiles for bridging carbido complexes, it should be stressed that the scattered examples of such complexes still remain rare. Furthermore, no computational interrogation has appeared other than an early extended Hückel MO treatment by Hoffmann<sup>[5]</sup> of  $[(\mu\text{-C})\{\text{Fe}(\text{TPP})\}_2]$  in which he predicted the viability of such a (diamagnetic) compound in advance of its discovery by Mansuy.<sup>[1]</sup> Given the importance of electronic communication between oxo bridges in all manner of

technological applications of metal oxides, this historical omission is surprising.

The serendipitous discovery of a symmetrical dirhenium carbido complex reported herein, has prompted us to devise a strategic synthesis. The remarkable simplicity of this complex also lends it to computational interrogation of the bonding without recourse to approximations that might otherwise cloud interpretations for more complex systems.

In a continuation of our studies of photogenerated half-sandwich  $\sigma$ -alkane complexes by NMR spectroscopy,<sup>[6]</sup> we have considered the possibility of including thiocarbonyl ligands in the co-ligand set. Photolysis of  $[\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{R})]$  ( $\text{R} = \text{H}$  (**1**),  $i\text{Pr}$ ) in alkane solvents afforded the first  $\sigma$ -alkane complexes with sufficient longevity for observation by cryoscopic NMR techniques.<sup>[7]</sup> We therefore turned our attention to Butler’s thiocarbonyl analogue  $[\text{Re}(\text{CS})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (**3**),<sup>[8]</sup> the photochemistry of which we will discuss elsewhere. In attempting to reproduce Butler’s original synthesis<sup>[8]</sup> from  $[\text{Re}(\text{thf})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (**2**),  $\text{CS}_2$ , and  $\text{PPh}_3$ , we did indeed obtain a modest yield of **3**, which was however contaminated with  $\text{Ph}_3\text{P}=\text{S}$  along with a new compound (**4**; Scheme 2). Small amounts of analytically pure **4**



**Scheme 2.** Synthesis of a dirhenium  $\mu$ -carbido complex (**4**;  $\text{Cp} = \eta\text{-C}_5\text{H}_5$ ).

could eventually be isolated using HPLC, and the identity was established by spectroscopic, microanalytical, and crystallographic data (see below) as the unusually simple  $\mu$ -carbido complex  $[(\mu\text{-C})\{\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$  (**4**).

The gross formulation of **4** followed from high-resolution electron-impact mass spectrometric data, whilst solution spectroscopic data ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR) suggested a local  $\text{C}_s$  geometry around the single rhenium chemical environment. The carbido resonance ( $\delta_{\text{C}} = 436.4$ )<sup>[9]</sup> was naturally the most conspicuous datum from the  $^{13}\text{C}$  NMR spectrum and this appears towards the downfield end of the range reported for

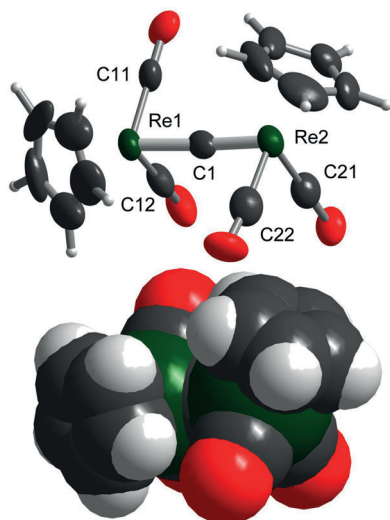
[\*] Dr. R. D. Young, Prof. Dr. A. F. Hill, Dr. G. E. Cavigliasso, Prof. Dr. R. Stranger  
Research School of Chemistry, Australian National University  
Acton, Canberra, ACT 0200 (Australia)  
E-mail: a.hill@anu.edu.au

[\*\*] This work was supported by the Australian Research Council (DP0557815 and DP1093516). The authors are grateful to the National Computational Infrastructure for access to the Australian National University supercomputer facilities.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201207731>.

the limited number of binuclear carbido ligands (Supporting Information, Table S1). For reasons to become apparent, it is also noteworthy that neither the single  $^{13}\text{C}$  resonance for the carbonyl ligands nor the  $^1\text{H}$  resonance for the cyclopentadienyl protons decoalesce or even broaden at temperatures above 180 K, suggesting either a high-symmetry static geometry ( $C_{2v}$  or  $C_i$ ) or a very low barrier to rotation about the  $\text{Re}=\text{C}=\text{Re}$  spine.

A crystal structure determination of **4** (Figure 1),<sup>[10]</sup> confirmed the formulation and also revealed that, at least in the solid state, the molecule adopts an approximate, but not crystallographically requisite,  $C_2$  geometry. If the molecule



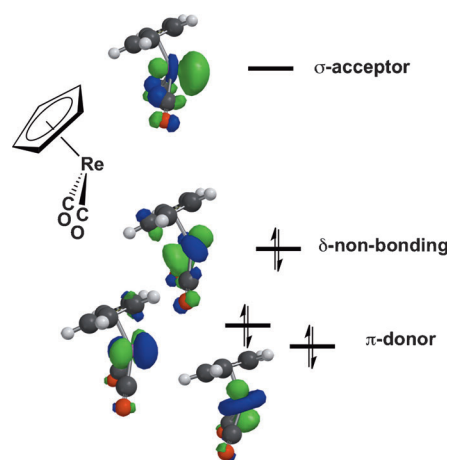
**Figure 1.** Molecular structure of **4** from a crystal (ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Re1–C1 1.882(14), Re2–C1 1.881(14); Re1–C1–Re2 173.3(7), C1–Re2–C21 90.7(6), C1–Re2–C22 88.2(6), C21–Re2–C22 88.6(7), C1–Re1–C11 86.4(6), C1–Re1–C12 89.6(6), C11–Re1–C12 87.2(6); C22–Re2...Re1–C11 172.7(6), C21–Re2...Re1–C12 –11.75(6).

were static in solution, this geometry would not be consistent with the higher symmetry suggested by NMR spectroscopic data ( $C_i$  or  $C_{2v}$ ) and so the chemical equivalence of carbonyl ligands and cyclopentadienyl rings must reflect a rapid dynamic process. The observation of four  $\nu_{\text{CO}}$  absorptions in the solution infrared spectrum of **4**, reflecting the slow exchange time domain, does not discriminate between the presence of a single low-symmetry rotamer or two coexistent rotamers of higher symmetry. The space-filling representation (Figure 1) gives a clue as to the origin, at least in part, of the stability of **4**, with access to the carbido atom being restricted. The geometries of the  $\{\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}$  termini are generally unremarkable for this fragment. In particular, the angles between the three monohapto ligands are all close to  $90^\circ$  and the molecule is unconstrained by any crystallographically imposed symmetry. The two almost colinear ( $173.3(7)^\circ$ ) rhenium–carbido bonds (1.882(14), 1.881(14) Å) fall within the range typical of Re–C multiple bonds;<sup>[11]</sup> for example,  $[\text{Re}(=\text{CHPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (1.95(2) Å),<sup>[11a]</sup>  $[\text{Re}(=\text{C}=\text{CHPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (1.912(14) Å),<sup>[11b]</sup>  $[\text{Re}(=\text{C}=\text{C}=\text{CPh}_2)(\text{SAd})(\text{NBu})_2]$  (1.898(13) Å),<sup>[11c]</sup> and  $[\text{Re}(\equiv\text{CPh})(\text{CO})_2-$

$(\eta\text{-C}_5\text{Me}_5)]^+$  (1.782(4) Å).<sup>[11d]</sup> For comparative purposes, complex **3** was also structurally characterized<sup>[12]</sup> and the thio-carbonyl ligand was found to have a similar Re–C bond length (1.866(9) Å).

The short Re–C separations suggest that **4** should be considered a class A carbido complex; however, the lack of any appreciable barrier to rotation about the  $\text{Re}=\text{C}=\text{Re}$  spine suggests a simple dimetallaallene isolobal analogy is misleadingly simplistic. Allenes have substantial barriers to rotation of the orthogonally disposed alkylidene termini about the central carbon (ca. 300 kJ mol $^{-1}$  for allene itself<sup>[13]</sup>), to the point that enantiomers may be resolved. This may be traced to coplanarity of the two  $\text{sp}^2$ -hybridized terminal carbon centers in the transition state, rendering one p orbital on the central carbon non-bonding. The bonding in **4** therefore calls for more detailed analysis to account for the free rotation about the dimetallacumulene spine. We have taken two approaches to this question. The first, for illustrative purposes, involves a qualitative consideration of the important bonding interactions between a carbon atom and two hypothetical  $\text{d}^6\text{ML}_5$   $\{\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}$  fragments (Figure 2). The mechanics of the second more rigorous approach (B88P86/TZP/ZORA) are deferred to the Supporting Information but serve to quantify the qualitative discussion presented here.

The combination of the (occupied)  $\text{C}_s$  and  $\text{Cp}_z$  orbitals with the  $\sigma$ -acceptor orbital on each rhenium establishes a 3-center, 4-electron  $\sigma$ -manifold. Each rhenium fragment has three occupied ( $\text{d}^6$ )  $t_{2g}$ -type orbitals, the lower two of which are near degenerate and spatially disposed to each retroactively interact with one of the two remaining orthogonal  $\text{Cp}_x$  and  $\text{Cp}_y$  orbitals, thereby setting up a further two orthogonal 3-center, 4-electron manifolds. In contrast to allenenes (3-center, 8-electron), the bonding in **4** is therefore best viewed as a 3-center, 12-electron system (Supporting Information, Figure S5). The corollary of this, coupled with the near degeneracy of the rhenium retrodative orbitals, is that rotation about the central carbon does not significantly disrupt the net  $\pi$ -bonding and any barrier to rotation is likely to be primarily steric in origin. A general feature of 3c–4e manifolds is that the HOMO has little central atom character,



**Figure 2.** Topology of the frontier orbitals of the  $\{\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}$  fragment, including their symmetry with respect to the Re–C vector.

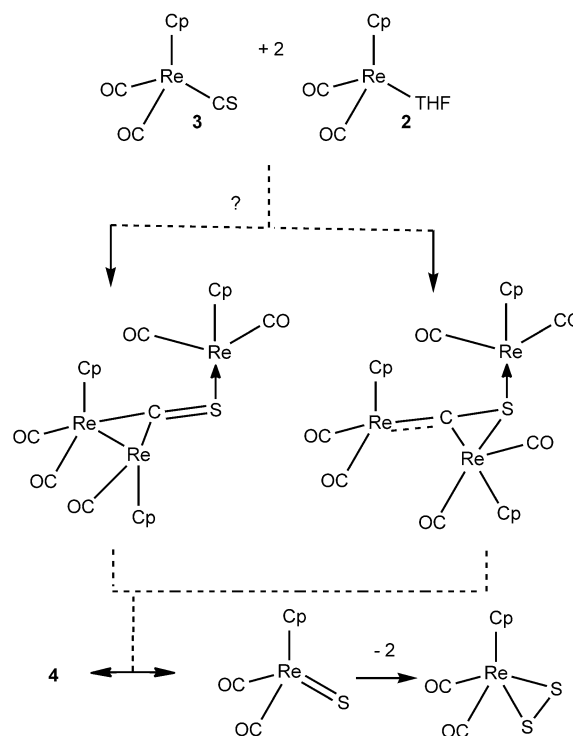
and this most likely contributes to the stability of **4** and lack of (carbido) ligand-centered reactivity. The LUMO and LUMO+1 do involve considerable central carbon character; however, the four CO ligands present alternative and more exposed sites for nucleophiles to attack.

The negligible barrier to rotation inferred experimentally and qualitatively rationalized above, may be computationally explored with recourse to DFT methods at the B88P86/TZP/ZORA level of theory (Supporting Information). Five minima were identified on the rotational energy surface corresponding to the  $C_2$  (compare with the observed geometry),  $C_1$ ,  $C_i$ ,  $C_{2h}$ , and  $C_{2v}$  geometries. The variance in the total bonding energies were negligible with the exception of the  $C_{2v}$  isomer, which lies some 15–16 kJ mol<sup>-1</sup> above the rest, which is primarily due to obstructive inter-ligand (Cp–Cp) interactions (see Figure 1). It should however be noted that full 360° rotation is not required for the CO and Cp environments to each appear chemically equivalent; this is satisfied by passing through the  $C_i$  conformer.

Subtracting the infrared spectrum of **1** from that **4** left a strong conspicuous absorption at 1019 cm<sup>-1</sup> (Nujol), presumed to correspond primarily to the  $B_1(\text{Re}=\text{C}=\text{Re})$  stretching mode ( $A_1$  is IR-silent). The calculated IR spectrum of **4** included the  $B_1(\text{Re}=\text{C}=\text{Re})$  mode at 1004 cm<sup>-1</sup>, allowing for the first time the assignment with confidence of a metal carbide vibrational mode. In contrast to the precursor **1**, which is colorless ( $\lambda = 255$  nm, primarily Re→CO MLCT), the carbido complex **4** is bright yellow, and it might be presumed that the metallacumulene is chromophoric. The observed and calculated UV/Vis spectra for **4** (Supporting Information;  $\lambda_{\text{max}} = 254, 263, 286$  nm) agree well allowing the absorptions to be interrogated with respect to the occupied and virtual valence orbitals available for electronic transitions. The absorption by **4** at 286 nm ( $\epsilon_{\text{obs}} \approx 10^8$  L mol<sup>-1</sup> m<sup>-1</sup>), which tails off into the visible region, thereby accounting for the color, primarily involves promotion to virtual orbitals of predominantly CO character. The higher-energy absorption ( $\lambda = 254$  nm), however, includes a significant component associated with promotion to the LUMO, which has considerable (38%) carbido Cp character (Supporting Information, Figure S6), and might therefore be described as partially ML<sub>carbido</sub>CT in nature, as all three transitions ( $\lambda = 286, 263, 254$  nm) exhibit significant MLCO plus MLC<sub>3</sub>H<sub>5</sub> CT character.

The mechanism by which **4** forms remains open to conjecture, given the intractable complexity of the reaction mixture. We can however provide some instructive circumstantial evidence. First, in a separate experiment, it can be shown that in the absence of light  $[\text{Re}(\text{CS})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (**3**) fails to react with PPh<sub>3</sub>; that is, phosphine does not directly abstract sulfur from the thiocarbonyl ligand to afford transient  $\{\text{Re}(\text{C})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}$ . Second, although **4** was initially only obtained in trace amounts, we find that when pre-isolated **3** is reintroduced to an excess of **2**, high yields (ca. 90% based on **3**) of **4** may be obtained along with a second complex, which was identified crystallographically as the disulfur complex  $[\text{Re}(\eta^2\text{-S}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (**5**) previously shown by Herberhold to arise from the reaction of **2** with elemental sulfur.<sup>[14]</sup>

We are therefore inclined to suspect that **4** arises from a di- or possible trinuclear intermediate with one or more extraneous  $[\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  fragments coordinating to the thiocarbonyl ligand, though the actual mode of CS bridging in such species is open to debate (Scheme 3). In support of this



**Scheme 3.** Mechanistic conjecture (in gray) to account for the reaction of **3** with **2** to give **4** and **5** (Cp =  $\eta\text{-C}_5\text{H}_5$ ).

we note that 1) Stone has described the reaction of **3** with  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_2]$  to afford  $[\text{RePt}(\mu\text{-CS})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ , the sulfur of which displays enhanced nucleophilic character relative to **3**;<sup>[15]</sup> 2) the coordination of two rhodium centers to the selenium of a selenocarbonyl ligand has recently been reported;<sup>[16]</sup> and 3) a tetrametallic molybdenum–iridium carbido complex has recently been shown to form by insertion of iridium(I) into the CSe bond of a selenocarbonyl ligand.<sup>[4e]</sup> The formation of carbido ligands by the abstraction of a chalcogen atom from a chalcocarbonyl ligand has recently assumed some significance for two reasons. First, terminal carbido complexes of ruthenium and osmium have been obtained by such a process.<sup>[17]</sup> Second, the biological chemistry community is currently at a loss to account for the biogenesis of the recently identified carbido ligand in the FeMo nitrogenase co-factor.<sup>[18]</sup> Both of these developments invite further investigations into the mechanisms of carbon–chalcogen cleavage reactions under mild conditions and molecular metal carbide chemistry more generally.

Received: September 25, 2012

Published online: February 19, 2013

**Keywords:** carbido complexes · metallacumulenes · rhenium · thiocarbonyl ligands

- [1] a) D. Mansuy, *Pure Appl. Chem.* **1980**, 52, 681; b) D. Mansuy, J.-P. Lecomte, J.-C. Chottard, J.-F. Bartoli, *Inorg. Chem.* **1981**, 20, 3119.
- [2] E. Solari, S. Antonijevic, S. Gauthier, R. Scopelliti, K. Severin, *Eur. J. Inorg. Chem.* **2007**, 367.
- [3] a) R. L. Miller, P. T. Wolczanski, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, 115, 10422; b) W. Beck, W. Knauer, C. Robl, *Angew. Chem.* **1990**, 102, 331; *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 318.
- [4] a) S. L. Latesky, J. P. Selegue, *J. Am. Chem. Soc.* **1987**, 109, 4731; b) M. Etienne, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1991**, 113, 2324; c) W. Knauer, W. Beck, *Z. Anorg. Allg. Chem.* **2008**, 634, 2241; d) S. H. Hong, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, 126, 7414; e) I. A. Cade, A. F. Hill, C. M. A. McQueen, *Organometallics* **2009**, 28, 6639; f) A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang, A. C. Willis, *Organometallics* **2009**, 28, 4394; g) A. F. Hill, M. Sharma, *Organometallics* **2012**, 31, 2538.
- [5] K. Tatsumi, R. Hoffmann, M.-H. Whangbo, *J. Chem. Soc. Chem. Commun.* **1980**, 509.
- [6] a) R. D. Young, A. F. Hill, W. Hillier, G. E. Ball, *J. Am. Chem. Soc.* **2011**, 133, 13806; b) R. D. Young, D. J. Lawes, A. F. Hill, G. E. Ball, *J. Am. Chem. Soc.* **2012**, 134, 8294.
- [7] a) S. Geftakis, G. E. Ball, *J. Am. Chem. Soc.* **1998**, 120, 9953; b) D. J. Lawes, S. Geftakis, G. E. Ball, *J. Am. Chem. Soc.* **2005**, 127, 4134.
- [8] I. S. Butler, N. J. Coville, D. Cozak, *J. Organomet. Chem.* **1977**, 133, 59.
- [9] Correlation of this peak to the  $\eta\text{-C}_5\text{H}_5$  proton resonances through a 2D HMBC experiment optimized for a 12 Hz C–H coupling (Supporting Information, Figure S1) confirmed that this peak was indeed due to the bridging carbido resonance.
- [10] Crystal data for **4**:  $\text{C}_{15}\text{H}_{10}\text{O}_4\text{Re}_2$ ,  $M_r = 626.64$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 8.1556(2)$ ,  $b = 20.0117(7)$ ,  $c = 9.8905(4)$  Å,  $\beta = 103.466(2)^\circ$ ,  $V = 1569.83(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.651$  Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 15.418$  mm<sup>-1</sup>,  $T = 200(2)$  K, orange plate,  $0.03 \times 0.03 \times 0.22$  mm<sup>3</sup>, 24490 reflections collected, 3593 unique data ( $2\theta \leq 55^\circ$ ),  $R_1 = 0.0326$  [for 1980 reflections with  $I > 2\sigma(I)$ ],  $wR_2 = 0.0919$ , 190 parameters.<sup>[19]</sup>
- [11] a) J. Chen, Y. Yu, K. Liu, G. Wu, P. Zheng, *Organometallics* **1993**, 12, 1213; b) D. A. Valyaev, O. V. Semeikin, M. G. Peterleitner, Y. A. Borisov, V. N. Khrustalev, A. M. Mazhuga, E. V. Kremer, N. A. Ustynyuk, *J. Organomet. Chem.* **2004**, 689, 3837; c) X. Li, M. Schopf, J. Stephan, J. Kippe, K. Harms, J. Sundermeyer, *J. Am. Chem. Soc.* **2004**, 126, 8660; d) C. P. Casey, S. Kraft, M. Kavana, *Organometallics* **2001**, 20, 3795.
- [12] Crystal data for **3**:  $\text{C}_8\text{H}_5\text{O}_2\text{ReS}$ ,  $M_r = 351.39$ , monoclinic,  $P2_1/m$ ,  $a = 6.7467(3)$ ,  $b = 9.3162(5)$ ,  $c = 7.0879(3)$  Å,  $\beta = 98.309(3)^\circ$ ,  $V = 440.82(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 2.647$  Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 13.970$  mm<sup>-1</sup>,  $T = 200(2)$  K, yellow prism,  $0.12 \times 0.23 \times 0.60$  mm<sup>3</sup>, 13631 reflections collected, 1056 unique data ( $2\theta \leq 54^\circ$ ),  $F^2$  refinement,  $R_1 = 0.0331$  [for 1035 reflections with  $I > 2\sigma(I)$ ],  $wR_2 = 0.0889$ , 62 parameters, 2 restraints.<sup>[19]</sup>
- [13] L. J. Schaad, *Tetrahedron* **1970**, 26, 4115.
- [14] M. Herberhold, D. Reiner, U. Thewalt, *Angew. Chem.* **1983**, 95, 1028; *Angew. Chem. Int. Ed. Engl.* **1983**, 22, 1000.
- [15] a) J. C. Jeffery, H. Razay, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1982**, 1733; b) J. C. Jeffery, H. Razay, F. G. A. Stone, *J. Chem. Soc. Chem. Commun.* **1981**, 243.
- [16] A. F. Hill, C. M. A. McQueen, *Organometallics* **2012**, 31, 2482.
- [17] a) S. R. Caskey, M. H. Stewart, J. E. Kivela, J. R. Sootsman, M. J. A. Johnson, J. W. Kampf, *J. Am. Chem. Soc.* **2005**, 127, 16750; b) M. H. Stewart, M. J. A. Johnson, J. W. Kampf, *Organometallics* **2007**, 26, 5102; c) Y. Mutoh, N. Kozono, M. Araki, N. Tsuchida, K. Takano, Y. Ishii, *Organometallics* **2010**, 29, 519.
- [18] a) T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. A. Andrada, E. Schleicher, S. Weber, D. C. Rees, O. Einsle, *Science* **2011**, 334, 940; b) K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann, S. DeBeer, *Science* **2011**, 334, 974.
- [19] CCDC 902444 (**3**) and CCDC 902445 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).