Formation and Structure of Heptacoordinate Dihalogeno Carbene-*C,O* Chelate Complexes and Dihalogeno Carbene-*C,O* Chelate Phosphine Complexes of Molybdenum(II) and Tungsten(II): A New Class of Fischer Type Carbene Complexes

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The carbene-*C,O* chelate carbonyl tungsten(0) complex [$(CO)_4W{=}C(OMe)C_6H_4OMe$-*o*] (**1**) reacts with phosphines by opening of the chelate ring to form [$(CO)_4(PR_3)W{=}C(OMe)C_6H_4$-OMe-*o*] (R = Me (**5**), ^{n}Bu (**6**), Ph (**7**), Cy (**8**)). Treatment of **5** and **6** with SnX_4 affords by oxidative decarbonylation, depending on R and X, either one or two isomers of the carbene-*C,O* chelate *di*carbonyl phosphine tungsten(II) complexes [$X_2(CO)_2(PR_3)W{=}C(OMe)C_6H_4OMe$-*o*] (R = Me, X = Cl (**9a**), Br (**9b**), I (**9c-A/9c-B**); R = ^{n}Bu, X = Cl (**10a**), Br (**10b-A/10b-B**), I (**10c**)). The isomers do not interconvert. In the corresponding reaction of **7** with $SnBr_4$ instead of a carbene-*C,O* chelate *di*carbonyl phosphine tungsten(II) complex the carbene-*C,O* chelate *tri*carbonyl tungsten(II) complex [$Br_2(CO)_3W{=}C(OMe)C_6H_4OMe$-*o*] (**3b**) is formed. When **8** is treated with $SnBr_4$, the formation of a carbene-*C,O* chelate phosphine tungsten-(II) complex cannot be detected any more. Like the *o*-OMe tungsten(0) complexes **5** and **6** the *p*-OMe tungsten(0) complex [$(CO)_4(P^nBu_3)W{=}C(OMe)C_6H_4OMe$-*p*] (**11**) and the ring-unsubstituted complex [$(CO)_4(P^nBu_3)W{=}C(OMe)Ph$] (**13**) react with $SnBr_4$ by oxidative decarbonylation and formation of W(II) complexes, [$Br_2(CO)_3(P^nBu_3)W{=}C(OMe)R'$] (R′ = C_6H_4OMe-*p*, Ph) (two isomers each). Dicarbonyl carbene-*C,O* chelate trimethylphosphine metal(II) complexes [$X_2(CO)_2(PMe_3)M{=}C(OMe)C_6H_4OMe$-*o*] (M = Mo, W; X = Cl, Br) are also accessible by substitution of PMe_3 for a CO ligand in [$X_2(CO)_3M{=}C(OMe)C_6H_4OMe$-*o*]. However, when PMe_3 is replaced by the bulkier PPh_3 in the reaction with [$Br_2(CO)_3$-$M{=}C(OMe)C_6H_4OMe$-*o*], instead of substitution, the opening of the chelate ring is observed.

Introduction

The oxidative decarbonylation of molybdenum or tungsten carbonyl complexes is a very common and well-known reaction. Typically, the hexacoordinate metal(0) center is oxidized by two units and one carbonyl ligand is replaced by two halides, resulting in heptacoordinate metal centers. Extensive studies in this field have been performed by Baker et al., and two reviews in this field have been published recently.[1]

Halogeno carbonyl complexes with additional carbene ligands are thought to play an important role as intermediates in the metathesis of olefins with halogeno carbonyl complexes as precursors.[2]

Usually, the oxidation of carbene carbonyl complexes leads to a cleavage of the metal−carbene bond and the former carbene ligand (a) dimerizes to give an olefin,[3] (b) is transformed into the corresponding carbonyl compound,[4] or (c) provides imidazolidin-2-ylidium salts (as has been observed in the reactions of some cyclic diamino-substituted group VI metal carbene complexes with iodine).[5] We recently observed that under certain conditions Fischer carbene complexes can be oxidized without cleavage of the metal−carbene bond, giving rise to the formation of rather rare metal(II) carbene complexes. Thus, the carbene-*C,O* chelate carbonyl complexes **1** and **2** are readily oxidized by tin(IV) halides or halogens to give the carbene-*C,O* chelate carbonyl

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(1) For recent reviews see: (a) Baker, P. K. *Adv. Organomet. Chem.* **1996**, *40*, 45−115. (b) Baker, P. K. *Chem. Soc. Rev.* **1998**, *27*, 125−131.

(2) (a) Bencze, L.; Markó, L. *J. Organomet. Chem.* **1971**, *28*, 271−272. (b) Bencze, L.; Markó, L. *J. Organomet. Chem.* **1974**, *69*, C19−C20. (c) Bencze, L.; Kraut-Vass, A.; Prókai, L. *J. Chem. Soc., Chem. Commun.* **1985**, 911−912. (d) Bencze, L.; Kraut-Vass, A. *J. Mol. Catal.* **1985**, *28*, 369−380.

(3) See, e.g.: (a) Le Bozek, H.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1462. (b) Moinet, C.; Le Bozek, H.; Dixneuf, P. H. *Organometallics* **1989**, *8*, 1493.

(4) See, e.g.: (a) Söderberg, B. C.; Bowden, B. A. *Organometallics* **1992**, *11*, 2220. (b) Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti Gerosa, A.; Cariati, F.; Bruni, S.; Moret, M.; Chiesi-Villa, A. *Inorg. Chim. Acta* **1994**, *220*, 233.

(5) Liu, S.-T.; Ku, R.-Z.; Liu, C.-Y.; Kiang, F.-M. *J. Organomet. Chem.* **1997**, *543*, 249.

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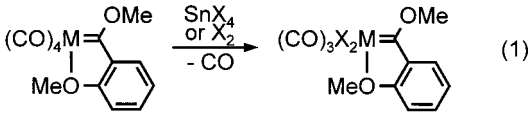
dihalogeno molybdenum and tungsten complexes **3a**−**c** and **4a,b**, respectively (eq 1).[6]



(1)

1, 2 **3a - c, 4a, b**

M = W (**1, 3**), Mo (**2, 4**)
X = Cl (**a**), Br (**b**), I (**c**)

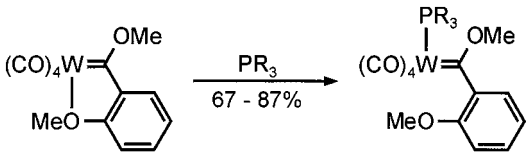
Neither the synthesis of a carbene-*C,O* chelate diiodo molybdenum complex nor that of carbene-*C,O* chelate dihalogeno *chromium* complexes could be achieved by this route.[6] When $SnCl_4$ was added to solutions of the carbene-*C,O* chelate tetracarbonyl chromium complex related to **1** and **2**, only a slow decomposition of the carbene complex and formation of $[Cr(CO)_6]$ was observed. Likewise, no reaction between $SnCl_4$ and the *nonchelating o*-anisylcarbene pentacarbonyl complex $[(CO)_5W{=}C(OMe)C_6H_4OMe\text{-}o]$ was observed. In contrast, $[(CO)_5W{=}C(OMe)Ph]$ did react with $SnCl_4$; however, the reaction afforded, among other products, a carbyne complex.[6]

From these observations it was concluded that an energetically high-lying HOMO at the metal is required for the oxidative decarbonylation of carbene carbonyl complexes by $SnCl_4$ or halogens.

Results

Synthesis of Carbene Phosphine Complexes. To test this hypothesis and to determine whether chelation is a prerequisite for the oxidative decarbonylation, nonchelating carbene tetracarbonyl phosphine complexes were assumed to be suitable starting complexes. In earlier studies, several carbene tetracarbonyl phosphine complexes were prepared either by thermolysis or by photolysis of carbene pentacarbonyl complexes in the presence of phosphines.[7]

The carbene tetracarbonyl phosphine complexes **5**−**8** were obtained by addition of phosphines to solutions of the carbene-*C,O* chelate carbonyl tungsten complex **1**, thus establishing that an opening of the chelate ring can be induced by nucleophiles. The complexes were formed almost quantitatively and, after column chromatography, were isolated in high yields (eq 2). Complex **7** has been prepared before.[8]



(2)

1 **5 - 8**

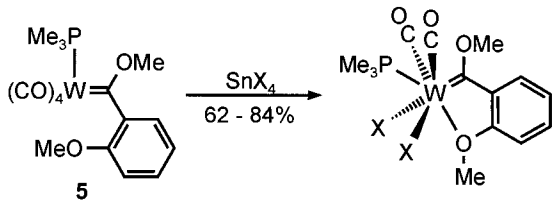
R = Me (**5**), ^{n}Bu (**6**), Ph (**7**), Cy (**8**)

The PCy_3 complex **8** was obtained as a mixture of the cis and the trans isomers (ratio ca. 4.5:1). All other complexes were formed highly stereoselectively, with the cis isomer being detected exclusively. In contrast, in earlier experiments the substitution of PR_3 for a CO ligand in *alkyl*carbene pentacarbonyl chromium and tungsten complexes was observed to afford mixtures of the cis and trans isomers. It was possible to separate the isomers by column chromatography. In solution above 30 °C a slow isomerization to form cis/trans mixtures again was obtained. The cis/trans equilibrium ratio was found to depend mostly on the steric requirements of the carbene and the phosphine ligand.[9]

At low temperature, alkylphosphines add to the carbene carbon atom of alkylcarbene complex to give ylide complexes.[10] The addition is reversible.[11] In contrast, there was no indication for the formation of ylide complexes when phosphines were added to solutions of **1**. Presumably, the equilibrium (carbene complex + PR_3)/ylide complex is too far on the side of the carbene complex for the ylide complexes to be detectable.

A molybdenum complex related to **7** was generated by Dötz et al. by reaction of **2** with PPh_3 at low temperature. The resulting carbene tetracarbonyl phosphine complex was labile and decomposed already below 0 °C to regenerate **2** and PPh_3.[12] When at room temperature PPh_3 was used in excess, the substitution of PPh_3 for a CO ligand was observed. In contrast, the complexes **5**−**8** are stable at room temperature.

Oxidation of the Carbene Phosphine Complexes. Similar to the carbene-*C,O* chelate complex **1** the trimethylphosphine complex **5** quickly reacted with $SnBr_4$ by evolution of a gas and formation of a white precipitate. As judged by the NMR spectrum of the solution, only one complex (**9b**) was formed quantitatively. It was not possible to purify the new compound **9b** by column chromatography, since it irreversibly adsorbed on silica. However, filtration through Celite (to remove the white solid $SnBr_2$) and recrystallization from CH_2Cl_2/pentane afforded pure **9b** in 84% yield (eq 3). Complex **9b** was also formed, in addition to other



(3)

5

X = Cl (**9a**), Br (**9b**)

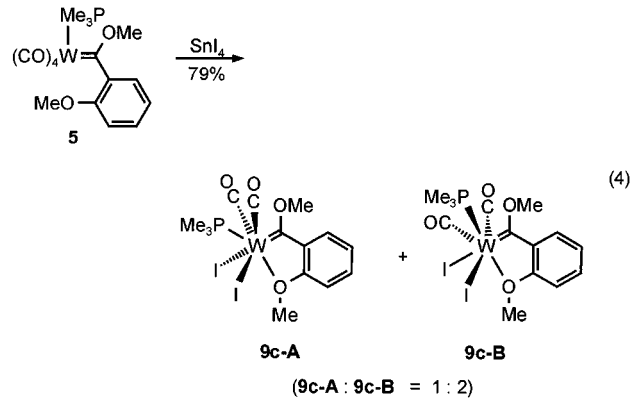
unidentified products, when **5** was treated with bromine in $CDCl_3$. However, it is more convenient to prepare **9b** by reaction of **5** with $SnBr_4$. This method gives somewhat higher yields, and the absence of byproducts facilitates purification of **9b**.

(6) Jaeger, M.; Stumpf, R.; Troll, C.; Fischer, H. *Chem. Commun.* **2000**, 931−932.
(7) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657−672.
(8) Jaeger, M. Dissertation, Universität Konstanz, 1993.
(9) (a) Fischer, E. O.; Fischer, H.; Werner, H. *Angew. Chem.* **1972**, *84*, 682−683; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 644−645. (b) Fischer, H.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 673−679.
(10) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262−1276.
(11) (a) Fischer, H.; Fischer, E. O.; Kreiter, C. G.; Werner, H. *Chem. Ber.* **1974**, *107*, 2459−2467. (b) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 309−317.
(12) Dötz. K. H.; Larbig, H.; Harms, K. *Chem. Ber.* **1992**, *125*, 2143-2148.

Analogously, addition of $SnCl_4$ to solutions of **5** led to the formation of complex **9a** (eq 3). Compound **9a** was not isolated but only identified by its IR and NMR spectra since, on a preparative scale, it was more easily accessible by a different route (vide infra). Surprisingly, two carbonyl ligands are lost in the course of the formation of **9a** and **9b** from **5** and SnX_4.

Both new complexes were characterized by IR and NMR spectroscopy, and complex **9b** was additionally characterized by a single-crystal X-ray analysis. However, the crystals were of only poor quality and the PMe_3 ligand was severely disordered. Therefore, a detailed discussion of the distances and angles in **9b** is not feasible. Nevertheless, the following structural features were unambiguously established. The PMe_3 ligand assumes a position almost trans to the coordinating OMe group. Complex **9b** contains a mirror plane which renders the two bromo and the two carbonyl ligands equivalent, in accord with the observation of only one ^{13}C resonance for the CO ligands.

The oxidative decarbonylation of **5** with SnI_4 deviated from those reactions involving $SnCl_4$ and $SnBr_4$. Instead of one complex, two new complexes were formed. It was not possible to separate them by crystallization, and attempted column chromatography led only to irreversible adsorption on silica. From the NMR spectrum of the reaction mixture and the elemental analysis of the isolated product mixture it followed that the oxidation of **5** with SnI_4 gave the two isomeric complexes **9c-A** and **9c-B** (eq 4). A rapid equilibration of the two isomers



(4)

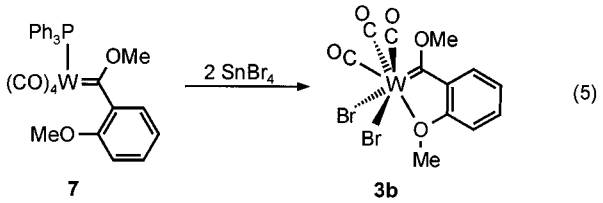
could be excluded, since the ratio remained unaffected when solutions of **9c-A** and **9c-B** were cooled or heated. The complexes **9c-A** and **9c-B** were also obtained in slightly different ratios (**9c-A**:**9c-B** is approximately 1:2) when the conditions for the reaction of **5** with SnI_4 were varied. A comparison of the IR spectra of **9c-A/9c-B** with those of the isomerically pure complexes **9a** and **9b** indicated that the structure of **9c-A** was similar to those of **9a** and **9b**. On the basis of the IR and NMR spectra the second isomer was assigned the structure **9c-B** (see eq 4).

Complex **5** did not react with iodine, even when iodine was employed in large excess. In contrast, addition of bromine to solutions of **5** in $CDCl_3$ gave **9b** by oxidative decarbonylation, in addition to some byproduct. The formation of byproducts has not been observed in the reaction of **5** with $SnBr_4$. Since oxidative decarbonylation of **5** by $SnBr_4$ also leads to somewhat higher yields of **9b**, it is more convenient to prepare **9b** from **5** and $SnBr_4$.

Similar to the case for **5**, the tributylphosphine complex **6** readily reacted with SnX_4 by oxidative decarbonylation and chelation. Again, the structure of the product complexes strongly depended on X. The reaction of **6** with $SnCl_4$ produced only one complex (**10a**), whose structure is similar to that of **9a**, **9b**, and **9c-A**. In contrast to **5**, treatment of **6** with $SnBr_4$ gave a mixture of two isomeric complexes, **10b-A** and **10b-B**, and in addition small amounts of a third unidentified complex. The mixture could not be separated. On the basis of the IR and NMR spectra **10b-A** was assigned a structure similar to those of **9a**, **9b**, **9c-A**, and **10a**. Isomer **10b-B** in turn is structurally related to **9c-B**. The complexes **10b-A** and **10b-B** were formed in the ratio **10b-A/10b-B** $\approx$ 2:1. Neither broadening nor a change in the relative intensities of the resonances in the ^1H NMR spectrum was observed when solutions of the isomeric mixture were warmed to 60 °C. Therefore, an interconversion of the isomers could be excluded.

The reaction of **6** with SnI_4 again afforded only one isomer. However, in contrast to **10a**, complex **10c** is structurally related to **9c-B** (Scheme 1).

When the steric requirements of the phosphine ligand were further increased, the reactions of the carbene tetracarbonyl phosphine complexes with tin tetrahalides took a different course. The reaction of the triphenylphosphine complex **7** with $SnBr_4$ in $CDCl_3$ did not afford a carbene-*C,O* chelate phosphine complex but rather the tricarbonyl complex **3b** (eq 5). Thus, in the



(5)

course of the reaction, instead of two carbonyl ligands, only one carbonyl and the phosphine ligand were replaced. Obviously, the very bulky PPh_3 (cone angle 145°) prevents the accommodation of seven ligands at the tungsten(II) atom in a stable arrangement.

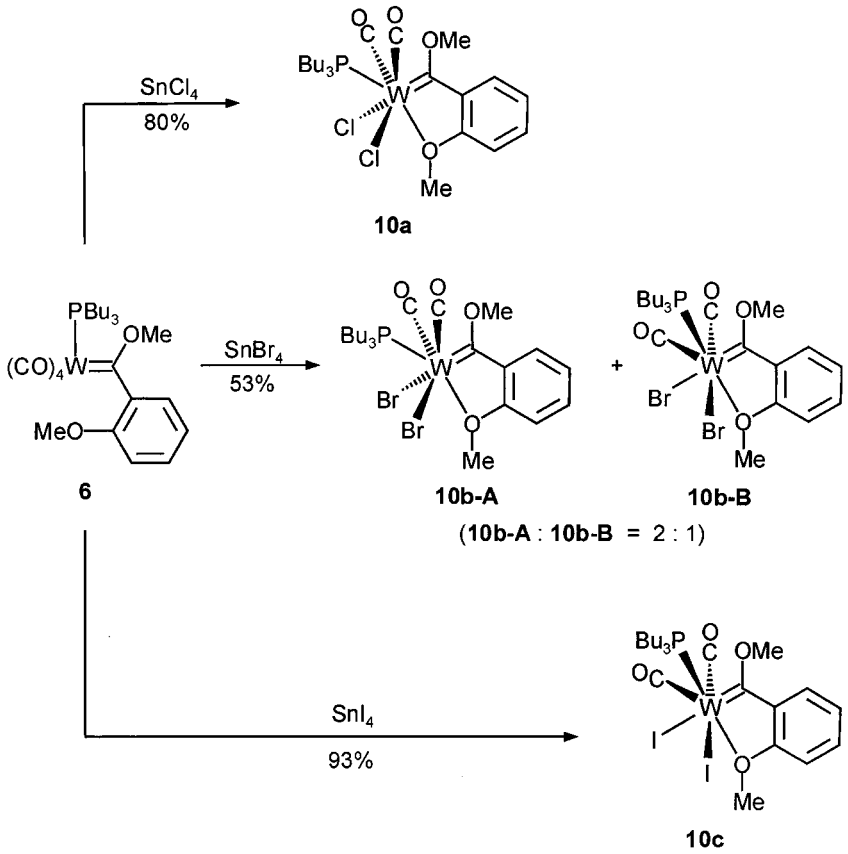
Complex **3b** was identified by comparison of its spectra with those of an authentic sample.[6] Two equivalents of $SnBr_4$ was required to drive the reaction to completion. One equivalent of $SnBr_4$ was consumed in the formation of the adduct $SnBr_4 \cdot PPh_3$, whose oxidation potential is insufficient to oxidize the carbene complex **7**. Adduct formation and thus reduction of the oxidation potential of SnX_4 also prevents the use of THF as the solvent. Tin tetrahalides are known to form with THF adducts, $[SnX_4(thf)_2]$.[13]

Like **7**, the ring-unsubstituted complex *cis*-$[(CO)_4(PPh_3)W{=}C(OMe)Ph]$ also reacted with $SnBr_4$. However, a dibromo carbene tungsten(II) complex could not be detected among the products. NMR analysis of the reaction mixture indicated loss of the carbene ligand from the complex.

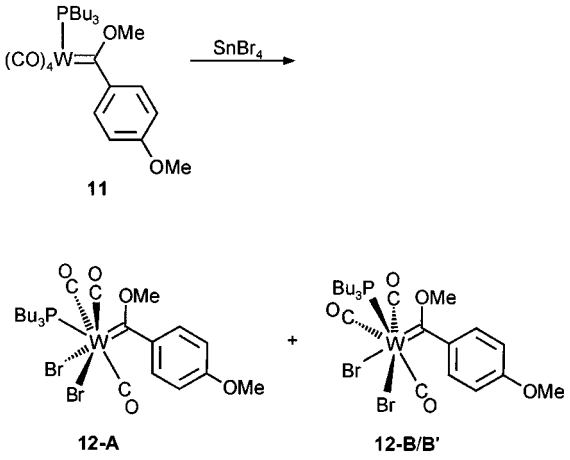
Chelation through a nucleophile such as, for example, OMe in **3b** seemed to be an important factor in stabilizing tungsten(II) carbene complexes. Therefore, we next

(13) See, e.g.: Wardell, J. L. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, U.K., 1994; Vol. 8, pp 4159−4171.

Scheme 1



investigated the reaction of $SnBr_4$ with the para-MeO-substituted complex *cis*-[$(CO)_4(P^nBu_3)W{=}C(OMe)C_6H_4$-OMe-*p*] (**11**)[9b] in which the PPh_3 has been replaced by the less sterically demanding and more strongly electron donating tri-*n*-butylphosphine. To prevent chelation, the *o*-MeO group has been shifted into the para position. In $CDCl_3$ **11** quickly reacted with $SnBr_4$ in excess. From the ^1H and the ^{31}P NMR spectra of the reaction solution the formation of three isomers (**12-A**, **12-B**, and **12-B′**, **12-B** and **12-B′** being conformers) in a ratio of approximately 2:1:1 could be deduced (eq 6).



(6)

The para-unsubstituted complex [$(CO)_4(P^nBu_3)$-$W{=}C(OMe)Ph$] (**13**) reacted similarly with $SnBr_4$. Two isomers of [$Br_2(CO)_3(P^nBu_3)W{=}C(OMe)Ph$] (**14-A** and **14-B**) were identified by NMR spectroscopy. The ratio (close to 1:1) was independent of whether the cis or the trans isomer of the starting complex **13** was employed.

From these observations it follows that chelation is not required for the formation of stable carbene tungsten(II) complexes. In addition to the two σ- and π-donating halides one strongly electron donating coligand such as P^nBu_3 suffices to stabilize carbene tungsten(II) complexes, provided there is no steric congestion at the W(II) center.

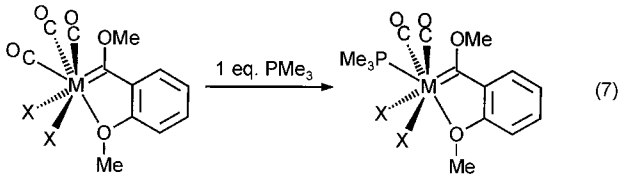
The failure to synthesize a dihalogeno carbene-*C,O* chelate tricyclohexylphosphine complex is thus readily explained by steric congestion at the metal. When $SnBr_4$ was added to a solution of the tricyclohexylphosphine complex **8** there was no indication for the formation of dihalogeno carbene-*C,O* chelate tungsten(II) complexes. The reaction mixture turned dark upon addition of the halide. Although a product could not be isolated, the IR spectrum of the reaction mixture indicated the formation of a carbyne complex, presumably *trans*-[$Br(CO)_4$-$W{\equiv}C(C_6H_4OMe$-*o*)].[14]

Reaction of Dihalogeno Carbene-*C,O* Chelate Complexes with Phosphines. The synthesis of carbene-*C,O* chelate phosphine complexes of molybdenum(II) from carbene carbonyl phosphine molybdenum(0) complexes and SnX_4 is not feasible, due to the lability of the molybdenum(0) starting complexes. An alternative approach to carbene-*C,O* chelate phosphine metal complexes would be substitution of PR_3 for a CO ligand in the readily available carbene-*C,O* chelate metal(II) complexes **3** and **4** (see eq 1). It has already been shown

(14) (a) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem.* **1973**, *85*, 619−621; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 564−565.

earlier that in tungsten halogeno carbonyl complexes one carbonyl ligand can be replaced by a phosphine ligand through substitution.[15] We therefore briefly studied the reactions of carbene-*C,O* chelate tricarbonyl dihalogeno complexes with phosphine.

The tungsten complexes **3a** and **3b** reacted with equimolar amounts of PMe_3 cleanly to give the dihalogeno carbene-*C,O* chelate phosphine complexes **9a** and **9b**, respectively, described above. This substitution approach could be extended to the corresponding molybdenum complexes. In NMR experiments it was possible to show that upon treatment of **4a** and **4b** with equimolar amounts of PMe_3 the molybdenum complexes **15a** and **15b** were readily and quantitatively formed. They were identified by their IR and NMR spectra, which are very similar to those of **9a** and **9b**. Therefore, similar structures were assigned to all four complexes (eq 7).



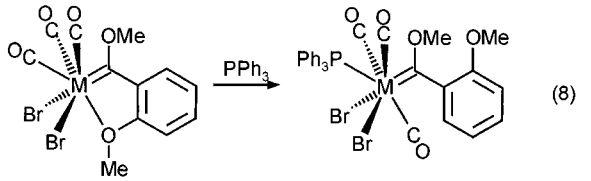
(7)

3a,**b**; **4a**,**b** **9a**,**b**; **15a**,**b**

M = W (**3**, **9**), Mo (**4**, **15**)
X = Cl (**a**), Br (**b**)

As expected on the basis of these previous results, the reaction of the chloro carbene-*C,O* chelate complex **3a** with P^nBu_3 also afforded a single isomer (**10a**), whereas the two isomeric products **10b-A** and **10b-B** in a ratio of 2.3:1 (see Scheme 1) were formed when the bromo carbene-*C,O* chelate complex **3b** was treated with P^nBu_3. Additional products were not observed. The ratio **10b-A**:**10b-B** was slightly larger as compared to that obtained by the oxidative decarbonylation route (Scheme 1).

The substitution pathway even made halogeno carbene triphenylphosphine complexes accessible. However, the phosphine did not displace a CO ligand but rather the coordinating MeO group of the chelate. Thus, the reactions of **3b** and **4b** with PPh_3 gave the nonchelating carbene phosphine complexes **16** and **17**, respectively (eq 8). The substitution of PPh_3 for a



(8)

3b, **4b** **16** (40%), **17** (56%)

M = W (**3b**, **16**), Mo (**4b**, **17**)

carbonyl ligand could not be observed. The products **16** and **17** were isolated from the reaction mixture as red powders. An excess of PPh_3 was necessary to drive the reaction of the molybdenum complex to a reasonable conversion. Nevertheless, the yields of isolated pure compounds were rather low (40 and 56%, respectively) due to their poor solubility. The complexes **16** and **17** were characterized by their IR and ^1H NMR spectra, which supported the structural proposal shown in eq 8. Very likely, steric congestion prevented the formation of halogeno carbene-*C,O* chelate dicarbonyl triphenylphosphine complexes.

(15) Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3565−3579.

Discussion

Reactions. Our experiments demonstrate that an opening of the chelate ring in the carbene-*C,O* chelate tungsten(0) complex **1** by nucleophiles is possible and that the resulting carbene phosphine complexes are stable and isolable species. The Mo analogue of **1** reacts similarly with PPh_3 at −40 °C; however, the ring opening is reversible. The species isolated at room temperature is not, as with **1**, a carbene tetracarbonyl phosphine complex but rather a product derived from substitution of PPh_3 for a CO ligand. The corresponding tungsten complex $[(CO)_3(PPh_3)W{=}C(OMe)C_6H_4OMe\text{-}o]$ is formed when solutions of **7** are irradiated in THF at −30 °C.[8]

The opening of the chelate in **1** requires strong nucleophiles such as phosphines. At room temperature complex **1** did not react with simple olefins such as 1-pentene, ethyl vinyl ether, vinyl acetate, malonic acid and fumaric acid dimethyl esters, and 2-methyl-1,3-butadiene.[8] Without a cocatalyst complex **1** is also inactive in the ring-opening metathesis polymerization of strained olefins such as norbornadiene, norbornene, and cyclopentene. When terminal alkynes are employed, polymerization of the alkyne is observed, albeit in low yield.[8]

The nonchelated carbene phosphine complexes **5** and **6** readily react with tin(IV) halides by oxidative decarbonylation to give halogeno carbene-*C,O* chelate carbonyl phosphine tungsten(II) complexes. Very likely the reaction proceeds in two steps: either (a) oxidation of the complex and replacement of one CO ligand by the halides is followed by dissociation of another W−CO bond and chelation or (b) loss of one CO ligand from **5** or **6** and chelation is followed by oxidation of the resulting carbene-*C,O* chelate complex and substitution of two halides for another CO ligand. Neither intermediate expected in these pathways could be detected spectroscopically. However, since the electron density and thus the W−CO back-bonding is reduced by oxidation of the metal, pathway a seems more likely. The assumption is supported by the stability of **5** and **6** at ambient temperature in the absence of SnX_4. These results indicate that chelation is not a prerequisite for an oxidative decarbonylation of **5** and **6** as long as the predominantly metal-centered HOMO is sufficiently high in energy. This can also be achieved by substitution of a phosphine for the chelating OMe group. The conclusion is supported by the successful oxidative decarbonylation of complex **11**. In the resulting carbene phosphine tungsten(II) complex the para position of the aryl−OMe substituent prevents chelation through OMe. Indeed, even the aryl-unsubstituted methoxy(phenyl)-carbene complex **13** is transferred into a W(II) carbene complex by $SnBr_4$. Apart from these complexes the oxidative decarbonylation of group 6 carbene carbonyl complexes has also been achieved by reaction of Br_2 with

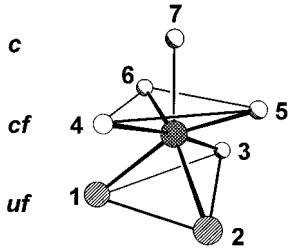


Figure 1.

some Lappert type carbene complexes in which the electron density at the metal is increased by the cyclic strongly electron donating bis(amino)carbene ligands $=C[N(R)-CH_2-]_2$.[16]

At first glance, the formation of the dibromo carbene-*C,O* chelate tricarbonyl complex instead of the expected dibromo carbene-*C,O* chelate dicarbonyl phosphine tungsten(II) complex **3b** in the reaction of the triphenylphosphine complex **7** with $SnBr_4$ is surprising. Very likely, the W−PPh_3 bond in $[Br_2(CO)_3(PR_3)W{=}C(OMe)C_6H_4$-OMe-*o*] (**16b**), initially formed in the reaction of **7** with PPh_3, is labile, as is also observed with $[(CO)_4(PR_3)$-$Mo{=}C(OMe)C_6H_4OMe$-*o*].[12] As a consequence, PPh_3 readily and reversibly dissociates from the metal. Trapping of free PPh_3 by $SnBr_4$ presumably is more rapid than readdition of PPh_3 to the metal. This interpretation agrees well with the requirement of 2 equiv of $SnBr_4$ for the complete conversion of **7** into **3b**. In the absence of the trapping agent $SnBr_4$ complex **16b** is stable and is readily accessible by opening of the chelate ring in **3b** by PPh_3 (see eq 8).

The failure to synthesize the initially expected dibromo carbene-*C,O* chelate dicarbonyl triphenylphosphine tungsten(II) complex as well as the corresponding tricyclohexylphosphine tungsten(II) complex is very likely due to steric congestion at the heptacoordinated tungsten atom. Bulky phosphines with large cone angles seem to prevent the formation of isolable heptacoordinated carbene-*C,O* chelate phosphine metal(II) complexes. This also explains why complex **3b** and the related molybdenum(II) complex react with PPh_3 by ring opening to form heptacoordinated nonchelated dibromo tricarbonyl carbene phosphine metal(II) complexes, whereas in the reaction of **3b** with PMe_3 dibromo carbene-*C,O* chelate dicarbonyl phosphine metal(II) complexes are obtained.

Structure. At least three different coordination polyhedra are conceivable for seven-coordinate complexes, the capped octahedron (co), the capped trigonal prism (ctp), and the pentagonal bipyramid (pbp). The heptacoordinated carbene complexes **3a**[6] and **9b** are best described by the co geometry. In the co geometry (Figure 1), three different positions can be identified: the unique capping position (*c*, 7), the 3-fold capped face (cf, 4−6), and the 3-fold uncapped face (*uf*, 1−3).

Haigh and Baker have used Pólya's theorem[17] to calculate the number of possible isomers in co structures for any combination of ligands, including symmetrical (L−L) and unsymmetrical (L−L′) chelating ligands. For the dihalogeno chelate carbene complexes of the type $[MX_2Y_3(L-L')]$, 48 pairs of enantiomers and 4 achiral (*meso*) isomers are conceivable; for the dihalogeno carbene-*C,O* chelate phosphine complexes $[MX_2Y_2Z$-$(L-L')]$ these numbers increase to 148 pairs of enantiomers and 4 achiral isomers.[18] The dihalogeno carbene-*C,O* chelate tricarbonyl complexes **3a**−**c** and **4a**,**c** (eq 1) and the dihalogeno carbene-*C,O* chelate dicarbonyl phosphine complexes **9a**−**c**, **10a**−**c**, and **15a**,**b** (eqs 3−5 and 7 and Scheme 1) are formed either as a single isomer or at least as mixtures of two isomers. Therefore, strong steric and/or electronic effects must be operating, leading to the preference for only a few structures. Hoffmann et al. gave a detailed account on seven-coordination based on EHMO calculations.[19] They identified the electronic factor that determines the preference of certain ligands for the different positions and provided some low-energy pathways for polytopal rearrangements. In d^4 complexes with co geometry, π-acceptor ligands prefer the *cf* over the *c* and the *uf* positions, while π donor ligands prefer the *uf* over the *c* and the *cf* positions. These predictions are partially fulfilled by the structures of **3a**[6] and **9b**, as determined by X-ray structural analyses. In both complexes two π-donor ligands (Cl, Br) occupy a *uf* position, whereas the third π-donor (OMe) is in a *cf* position. The remaining two *cf* positions are occupied, as expected by the strong π-acceptors CO. In both complexes the π-acceptor $C_{carbene}$ is in the *c* position, thus forcing the OMe substituent into the "unfavorable" *cf* position. In contrast to the case for **3a**, the structure of the corresponding iodo carbene-*C,O* chelate complex **3c** agrees with the predictions: all π-donor ligands (I^- and OMe) are in the *uf* position. The π-acceptor ligands are at either the *cf* or the *c* position, $C_{carbene}$ occupying a *cf* position. The **A** structure of **9c** and **10b** corresponds to that of **9b**. The detailed geometry of the **B** type isomer is at present unknown. Several structures derived from **A** are conceivable. From the ^{13}C NMR spectra it follows that both CO ligands are inequivalent. Except for $C_{carbene}$ and OMe, all mutual changes of the positions of two unlike ligands in these complexes will render the two CO ligand inequivalent. Since the **A** and the **B** isomers do not interconvert and since the product ratio **A**:**B** depends on the reaction conditions, both isomers are formed in parallel pathways. Considering this and the increasing preference for isomer **B** in the series **9a**−**c** and **10a**−**c,** the structure of isomer **B** very likely is derived from that of **3c**[20] by substitution of PR_3 for a CO ligand: both halides and the OMe substituent occupy the *uf* position and at least one CO ligand and $C_{carbene}$ the *cf* position. PR_3 then resides either in the remaining *cf* position or in the *c* position. The increasing preference for isomer B in the series **9a**−**c** and **10a**−**c** is presumably due to increasing steric demand of the different ligand (Cl, Br, I and PMe_3, P^nBu_3).

Experimental Section

General Considerations. All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl or CaH_2 and were freshly distilled prior to use. The silica

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gel used for chromatography (J. T. Baker, silica gel for flash chromatography) was dried in vacuo and saturated with nitrogen. The yields refer to analytically pure compounds and were not optimized. The complexes **1**,[21] **3a**,[6] **3b**,[6] **4a**,[6] **4b**,[6] and **13**[7] were prepared according to literature procedures. Complex **11** was prepared as described in ref 4 for **13.** Acetyl bromide was purchased from Fluka. Instruments used were as follows: IR, FT-IR spectrophotometer, Bio-Rad; ^{1}H NMR and ^{13}C NMR, Bruker WM 250, Bruker AC 250, JEOL JNX 400; ^{31}P NMR, JEOL JNX 400; MS, Finnigan MAT 312 (EI) or Finnigan MAT 312/AMD5000 (FAB). All spectra were recorded at room temperature. Unless specifically mentioned, chemical shifts are reported relative to TMS (^{1}H NMR spectra), to the residual solvent peaks (^{13}C NMR spectra; $CDCl_3$ δ 77.0, CD_2Cl_2 δ 53.8, acetone-d_6 δ 206.6), or to external H_3PO_4 (^{31}P NMR spectra).

***cis*-Tetracarbonyl[methoxy(*o*-methoxyphenyl)carbene](trimethylphosphine)tungsten(0) (5).** At room temperature, 140 μL (0.10 g, 1.4 mmol) of PMe_3 was added by syringe to a solution of **1** (0.61 g, 1.3 mmol) in 25 mL of CH_2Cl_2. The solution turned red. The solvent was removed in vacuo, and the residue was chromatographed on silica at −30 °C. With pentane/CH_2Cl_2 (ratio decreasing from 5:1 to 1:5) a red-orange fraction was eluted. After removal of the solvent, the residue solidified to give a red crystalline mass, yield 0.51 g (0.98 mmol, 72%). Mp: 71 °C. IR (pentane): ν(CO) 2023 m, 1924 s, 1907 vs, 1892 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.55 (d, J_{PH} = 7.9 Hz, 9H, PMe_3), 3.77 (s, 3H, aryl OMe), 4.12 (s, 3H, carbene OMe), 6.82−6.85 (m, 1H, aryl H), 6.97−6.99 (m, 2H, aryl H), 7.17−7.24 (m, 1H, aryl H). ^{13}C NMR ($CDCl_3$): δ 20.9 (d, J_{PC} = 27.6 Hz, PMe_3), 54.8 (s, aryl OMe), 65.2 (s, carbene OMe), 110.4, 120.1, 124.6, 128.8, 145.2, 149.2 (6s, aryl C), 202.5 (d, J_{PC} = 7.7 Hz, 2CO), 207.4 (d, J_{PC} = 19.3 Hz, CO), 213.2 (d, J_{PC} = 7.8 Hz, CO), 320.9 (d, J_{PC} = 7.4 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ −32.9 (s and d, J_{PW} = 230 Hz). MS/EI (70 eV, 100 °C); *m*/*z* (%) 522 (40) [M$^+$], 494 (20) [M$^+$ − CO], 466 (35) [M$^+$ − 2CO], 438 (100) [M$^+$ − 3CO], 410 (80) [M$^+$ − 4CO]. Anal. Calcd for $C_{16}H_{19}O_6PW$ (522.2): C, 36.80; H, 3.67. Found: C, 36.62; H, 3.71.

***cis*-Tetracarbonyl[methoxy(*o*-methoxyphenyl)carbene](tri-*n*-butylphosphine)tungsten(0) (6).** Preparation and purification of **6** were carried out analogously to **5**. However, to avoid separation problems on chromatography, only 0.9 equiv of P^nBu_3 was used. Complex **6** was obtained as a red powder (86%). Mp: 44 °C. IR (pentane): ν(CO) 2020 m, 1920 s, 1904 vs, 1890 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, J_{HH} = 6.9 Hz, 9H, PBu_3), 1.30−1.43 (m, 12H, PBu_3), 1.70−1.79 (m, 6H, PBu_3), 3.77 (s, 3H, aryl OMe), 4.02 (s, 3H, carbene OMe), 6.81−6.85 (m, 1H, aryl H), 6.97−7.02 (m, 2H, aryl H), 7.18−7.25 (m, 1H, aryl H). ^{13}C NMR ($CDCl_3$): δ 13.8 (s, PBu_3), 24.3 (d, J_{PC} = 12.8 Hz, PBu_3), 25.9 (s, PBu_3), 29.1 (d, J_{PC} = 23.9 Hz, PBu_3), 54.9 (s, aryl OMe), 64.3 (s, carbene OMe), 110.3, 120.0, 124.9, 128.8, 144.6, 149.1 (6 s, aryl C), 202.8 (d, J_{PC} = 8.2 Hz, 2CO), 206.9 (d, J_{PC} = 19.3 Hz, CO), 213.6 (d, J_{PC} = 8.1 Hz, CO), 321.2 (d, J_{PC} = 7.4 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ −3.15 (s and d, J_{PW} = 230 Hz). MS/EI (70 eV, 100 °C): *m*/*z* (%) 648 (12) [M$^+$], 620 (3) [M$^+$ − CO], 592 (13) [M$^+$ − 2CO], 564 (28) [M$^+$ − 3CO], 536 (5) [M$^+$ − 4CO], 446 (9) [M$^+$ − PBu_3], 362 (28) [M$^+$ − PBu_3 − 3CO], 202 (22) [PBu_3^+]. Anal. Calcd for $C_{25}H_{37}O_6PW$ (648.4): C, 46.31; H, 5.75. Found: C, 46.02; H, 5.71.

***cis*-Tetracarbonyl[methoxy(*o*-methoxyphenyl)carbene](triphenylphosphine)tungsten(0) (7).** A 1.6 g portion (6.1 mmol) of PPh_3 was added to a solution of **1** (0.90 g, 2.0 mmol) in 50 mL of CH_2Cl_2. The initially brown solution turned slowly red. The solvent was removed in vacuo after 30 min, and the residue was chromatographed at −40 °C with pentane/CH_2Cl_2 (ratio decreasing from 5:1 to 2:1). Removal of the solvent gave a light red powder. Recrystallization from pentane/CH_2Cl_2 (1:1) afforded 1.2 g (87%) of complex **7** as light-red crystals. Mp: 125 °C. IR (pentane): ν(CO) 2025 m, 1936 vs, 1926 sh, 1911 vs, 1897 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.47 (s, 3H, aryl OMe), 3.98 (s, 3H, carbene OMe), 6.34 (dd, J = 7.3 and 1.5 Hz, 1H, C_6H_4), 6.72 (m, 2H, C_6H_4), 7.12 (ddd, J = 8.1, 7.6, and 1.5 Hz, 1H, C_6H_4), 7.4 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$, −10 °C): δ 54.7 (s, aryl OMe), 65.4 (s, carbene OMe), 110.2, 119.4, 123.0, 128.2, 128.7, 129.8, 133.2, 135.7, 136.3, 149.6 (aryl C), 202.5 (d, J_{PC} = 28.8 Hz, CO), 205.8 (d, J_{PC} = 10.2 Hz, CO), 212.8 (d, J_{PC} = 10.2 Hz, CO), 320.2 (d, J_{PC} = 7.1 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ −3.15 (s and d, J_{PW} = 230 Hz). MS/EI (FAB): *m*/*z* (%) 708 (17) [M$^+$], 680 (16) [M$^+$ − CO], 652 (100) [M$^+$ − 2CO], 624 (57) [M$^+$ − 3CO], 596 (47) [M$^+$ − 4CO], 581 (56) [M$^+$ − 4CO − CH_3], 445 (57) [M$^+$ − PPh_3]. Anal. Calcd for $C_{31}H_{25}O_6PW$ (708.4): C, 52.56; H, 3.56. Found: C, 52.59; H, 3.61.

Tetracarbonyl[methoxy(*o*-methoxyphenyl)carbene](tricyclohexylphosphine)tungsten(0) (8). The preparation and purification of **8** were carried out analogously to **5**. Complex **8** was obtained as a mixture of the cis and trans isomers (ratio: ca. 4.5:1) as a red-orange powder. Yield: 67%. IR (pentane): ν(CO) 2018 m, 1918 m, 1910 vs, 1899 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22−1.94 (m, 33H, PCy_3), 3.77 and 3.78 (2 s, 3H, aryl OMe, cis and trans), 3.85 and 4.30 (2 s, 3H, carbene OMe, cis and trans), 6.80−7.26 (m, 4H, aryl H). ^{13}C NMR ($CDCl_3$): δ 26.4, 27.6, 27.7, 27.9, 30.1, 37.2, 37.4 (s, PCy_3), 54.9 and 55.3 (2 s, aryl OMe), 63.3 and 65.1 (2 s, carbene OMe), 109.9, 110.8, 119.7, 120.0, 122.2, 125.7, 127.6, 129.0, 143.1, 147.0, 148.7, 150.2 (12s, aryl C), 204.1 (d, J_{PC} = 6.7 Hz, CO), 205.2 (d, J_{PC} = 6.0 Hz, CO), 206.8 (d, J_{PC} = 21 Hz, CO), 214.5 (d, J_{PC} = 7.8 Hz, CO), carbene C not found. ^{31}P NMR ($CDCl_3$): δ 34.2 (s and d, J_{PW} = 230 Hz) and 30.8 (s and d, J_{PW} not found). Anal. Calcd for $C_{31}H_{43}O_6PW$ (726.5): C, 51.25; H, 5.97. Found: C, 51.0; H, 5.90.

Dicarbonyldichloro[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](trimethylphosphine)tungsten(II) (9a). A 7.0 mL portion (1.0 mmol) of a dilute solution of PMe_3 (0.145 M in CH_2Cl_2) was added to a vigorously stirred solution of 0.49 g (1.0 mmol) of **3a** in 25 mL of CH_2Cl_2. The mixture was stirred for 10 min. The volume of the solution was then reduced in vacuo to ca. 10 mL. A layer of 10 mL of pentane was placed on top of this solution. When the mixture was cooled to −30 °C, small red crystals formed overnight. Yield: 0.34 g (0.63 mmol, 62%). Mp: 140 °C dec. IR (CH_2Cl_2): ν(CO) 1970 m, 1888 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.94 (d, J_{PH} = 10.7 Hz, 9H, PMe_3), 4.39 (s, 3H, carbene OMe), 4.84 (s, 3H, aryl OMe), 7.19−7.35 (m, 2H, aryl H), 7.50−7.53 (m, 1H, aryl H), 7.76−7.80 (m, 1H, aryl H). ^{13}C NMR (CD_2Cl_2, −80 °C): δ 15.3 (d, J_{PC} = 37.4 Hz, PMe_3), 61.2 (s, carbene OMe), 62.4 (s, aryl OMe), 110.4, 122.3, 122.7, 133.6, 133.8, 161.1 (6s, aryl C), 223.0 (d, J_{PC} = 21.8 Hz and dd, J_{PC} = 20.0 Hz and J_{WC} = 133 Hz, CO), 274.0 (dd, J_{PC} = 13.2 Hz, J_{WC} not found, carbene C). ^{31}P NMR ($CDCl_3$): δ −10.4 (s and d, J_{PW} = 223 Hz). Anal. Calcd for $C_{14}H_{19}Cl_2O_4PW$ (537.0): C, 31.31; H, 3.57. Found: C, 30.88; H, 3.60.

Dibromodicarbonyl[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](trimethylphosphine)tungsten(II) (9b). A 1.3 g amount (2.9 mmol) of $SnBr_4$ was added in small portions to a solution of 1.5 g (2.9 mmol) of **5** in 40 mL of CH_2Cl_2. The solution was stirred for 30 min and then filtered through a layer of Celite. The volume of the solution was reduced to 10 mL. A layer of 10 mL of pentane was placed on top of this solution. When this mixture was cooled to −30 °C, red crystals formed overnight. They were collected by filtration and dried in vacuo. Yield: 1.5 g (2.4 mmol, 84%). Mp: 140 °C dec. IR (CH_2Cl_2): ν(CO) 1972 m, 1892 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.00 (d, J_{PH} = 10.7 Hz, 9H, PMe_3), 4.41 (s, 3H, carbene OMe), 4.95 (s, 3H, aryl OMe), 7.18−7.37 (m, 2H, aryl H), 7.37−7.58 (m, 1H, aryl H), 7.79−7.83 (m, 1H, aryl H). ^{13}C NMR ($CDCl_3$, −20 °C): δ 17.6 (d, J_{PC} = 37.3 Hz, PMe_3), 62.6 (s, carbene OMe), 63.5 (s, aryl OMe), 110.8, 122.8, 123.2, 134.1, 134.2,

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162.1 (6s, aryl C), 219.8 (d, J_{PC} = 20.9 Hz and dd, J_{PC} = 21.0 Hz and J_{WC} = 135 Hz, CO), 273.9 (dd, J_{PC} = 13.6 Hz, J_{WC} not found, carbene C). ^{13}C NMR (CH_2Cl_2, −80 °C): δ 16.9 (d, J_{PC} = 38.3 Hz, PMe_3), 62.5 (s, carbene OMe), 63.5 (s, aryl OMe), 110.7, 122.8, 133.5, 134.0, 161.7 (5s, aryl C), 220.1 (d, J_{PC} = 20.7 Hz and dd, J_{PC} = 20.6 Hz and J_{WC} = 136 Hz, 2CO), 272.9 (dd, J_{PC} = 12.9 Hz, J_{WC} not found, carbene C). ^{31}P NMR ($CDCl_3$): δ −16.7 (s and d, J_{PW} = 215 Hz). Anal. Calcd for $C_{14}H_{19}Br_2O_4PW$ (625.9): C, 26.86; H, 3.06. Found: C, 26.64; H, 3.12.

Dicarbonyldiiodo[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](trimethylphosphine)tungsten(II) (9c-A/9c-B). A 0.88 g amount (1.4 mmol) of SnI_4 was added in small portions to a solution of 0.75 g (1.4 mmol) of **5** in 50 mL of CH_2Cl_2. Immediately, a gas evolved and a voluminous yellow precipitate formed. The solution was stirred for 10 min and then filtered through a layer of Celite. The volume of the red solution was reduced to ca. 5−10 mL. A layer of 10 mL of pentane was placed on top of this solution. When the mixture was cooled to −30 °C, red crystals formed overnight. They were collected by filtration and dried in vacuo. Yield: 0.81 g (1.1 mmol, 79%). The red crystalline material consisted of both isomers **9c-A** and **9c-B** (ratio: ca. 1:2). IR (CH_2Cl_2): ν(CO) 1964 vs (**A** and **B**), 1896 m (**A**), 1865 s (**B**) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.57 and 2.09 (2 d, J_{PH} = 9.7 and 10.3 Hz, 9H, PMe_3 of **B** and **A**), 4.43 and 4.53 (2 s, 3H, carbene OMe of **A** and **B**), 4.95 and 5.08 (2 s, 3H, aryl OMe of **B** and **A**), 7.18−7.40 (m, 2H, aryl H of **A**/**B**), 7.56−7.62 (m, 1H, aryl H of **A**/**B**), 7.72−7.76 (m, 1H, aryl H of **A**/**B**). ^{13}C NMR ($CDCl_3$, −20 °C): δ 16.3 (d, J_{PC} = 35.4 Hz, PMe_3 of **B**) 20.1 (d, J_{PC} = 39 Hz, PMe_3 of **A**), 62.6 (s, carbene OMe of **A**), 66.2 (s, carbene OMe of **B**), 67.3 (s, aryl OMe of **B**), 67.9 (s, aryl OMe of **A**), 111.2, 122.8, 123.2, 134.4, 135.5, 163.1 (6 s, aryl C of **A**), 113.3, 123.1, 124.7, 133.0, 135.5, 163.1 (6 s, aryl C of **B**) 215.5 (d, J_{PC} = 20.7, 2CO of **A**), 227.9 (d, J_{PC} = 7.3, CO of **B**), 245.6 (d, J_{PC} = 30.5, CO of **B**), 273.2 (d, J_{PC} = 13.4, carbene C of **A**), 301.0 (d, J_{PC} = 6.1 Hz, carbene C of **B**). ^{31}P NMR ($CDCl_3$): δ −11.45 (s and d, J_{PW} = 237 Hz, **B**) and δ −23.65 (s and d, J_{PW} = 210 Hz, **A**). Anal. Calcd for $C_{14}H_{19}I_2O_4PW$ (719.0): C, 23.36; H, 2.66. Found: C, 23.56; H, 2.61.

Dicarbonyldichloro[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](tri-*n*-butylphosphine)tungsten(II) (10a). A freshly prepared diluted solution of 0.18 g (0.23 mL, 0.89 mmol) of tri-*n*-butylphosphine in 10 mL of CH_2Cl_2 was slowly added to a vigorously stirred solution of 0.45 g (0.9 mmol) of **3a** in 25 mL of CH_2Cl_2. The solution was stirred for 10 min and then filtered through a layer of Celite. The volume of the solution was reduced to 10 mL. A layer of 10 mL of pentane was placed on top of this solution. When the mixture was cooled to −30 °C, red crystals of **10a** formed overnight. They were collected by filtration and dried in vacuo. Yield: 0.48 g (0.72 mmol, 80%). Mp: 177 °C dec. IR (CH_2Cl_2): ν(CO) 1968 m, 1886 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, J_{HH} = 7.2 Hz, 9H, PBu_3), 1.39−1.58 (m, 6H, PBu_3), 1.61−1.72 (m, 6H, PBu_3), 2.22−2.32 (m, 6H, PBu_3), 4.39 (s, 3H, carbene OMe), 4.75 (s, 3H, aryl OMe), 7.14−7.21 (m, 1H, aryl H), 7.26−7.29 (m, 1H, aryl H), 7.46−7.53 (m, 1H, aryl H), 7.73−7.77 (m, 1H, aryl H). − ^{13}C NMR ($CDCl_3$): δ 13.6 (s, PBu_3), 24.1 (d, J_{PC} = 13.4 Hz, PBu_3), 25.4 (d, J_{PC} = 10.4 Hz, PBu_3), 25.6 (d, J_{PC} = 14.6 Hz, PBu_3), 60.5 (s, carbene OMe), 62.5 (s, aryl OMe), 110.6, 122.8, 123.8, 133.2, 133.9, 161.5 (6 s, aryl C), 222.1 (d, J_{PC} = 18.8 Hz and dd, J_{PC} = 18.8 Hz and J_{WC} = 133 Hz, 2CO), 321.2 (d, J_{PC} = 12.5 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ 2.74 (s and d, J_{PW} = 223 Hz). Anal. Calcd for $C_{23}H_{37}Cl_2O_4PW$ (663.3): C, 41.65; H, 5.62. Found: C, 42.05; H, 5.85.

Dibromodicarbonyl[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](tri-*n*-butylphosphine)tungsten(II) (10b-A/10b-B). The synthesis of **10b-A/10b-B** from 0.54 g (0.83 mmol) of **6** and $SnBr_4$ (17 mL, 0.83 mmol, 0.048 M in CH_2Cl_2) was carried out analogously to that of **9c-A/9c-B** from **5** and SnI_4. A red-brown powder was obtained, consisting of both isomers **10b-A** and **10b-B** (ratio: ca. 2:1). Yield: 0.33 g (0.44 mmol, 53%). IR (CH_2Cl_2): ν(CO) ∼1960 vs (**A** and **B**), 1890 vs (**A**), 1859 s cm^{-1} (**B**). ^{1}H NMR ($CDCl_3$): δ 0.77 and 0.96 (2 t, J_{PH} = 7.3 and 7.2 Hz, 9H, PBu_3 of **B** and **A**), 1.10−1.78 (m, 12H, PBu_3 of **A**/**B**), 2.17−2.67 (m, 6H, PBu_3 of **A**/**B**), 4.39 and 4.63 (2 s, 3H, carbene OMe of **A** and **B**), 4.68, 4.84, and 4.87 (3 s, 3H, aryl OMe of **A**, **B**, and **B′**), 7.09−7.23 (m, 2H, aryl H of **A**/**B**), 7.30−7.68 (m, 1H, aryl H of **A**/**B**), 7.78−7.88 (m, 1H, aryl H of **A**/**B**). ^{13}C NMR ($CDCl_3$, −20 °C; only the resonances of isomer **A** could be assigned unambiguously): δ 13.8 (s, PBu_3), 24.0 (d, J_{PC} = 14.0 Hz, PBu_3), 25.4 (d, J_{PC} = 4.6 Hz, PBu_3), 26.3 (d, J_{PC} = 30 Hz, PBu_3), 61.0 (s, carbene OMe), 63.1 (s, aryl OMe), 111.5, 122.4, 124.7, 127.7, 135.3, 161.7 (6 s, aryl C), 218.3 (d, J_{PC} = 18.8 Hz and d, J_{PC} = 19.1 Hz, 2CO), 272.7 (d, J_{PC} = 12.6 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ 15.2 (s and d, J_{PW} = 230 Hz, **A**), 2.8 (s and d, J_{PW} = 223 Hz, **B**), 2.7 (s and d, J_{PW} = 223 Hz, **B′**). Molecular formula: $C_{23}H_{37}Br_2O_4PW$ (752.2).

Dicarbonyldiiodo[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](tri-*n*-butylphosphine)tungsten(II) (10c). The synthesis of **10c** from 0.65 g (1.0 mmol) of **6** in 50 mL of CH_2Cl_2 and SnI_4 (0.63 g, 1.0 mmol) was carried out analogously to that of **9c-A/9c-B** from **5** and SnI_4. Yield: 0.79 g (0.93 mmol, 93%) of red crystals. Mp: 185 °C dec. IR (CH_2Cl_2): ν(CO) 1954 vs, 1863 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.78 (t, J_{PH} = 7.3 Hz, 9H, PBu_3), 0.81−1.35 (2m, 12H, PBu_3), 1.63−1.81 (m, 3H, PBu_3), 2.36−2.51 (m, 3H, PBu_3), 4.51 (s, 3H, carbene OMe), 4.94 (s, 3H, aryl OMe), 7.21−7.34 (m, 2H, aryl H), 7.51−7.58 (m, 1H, aryl H), 7.71−7.75 (m, 1H, aryl H). ^{13}C NMR ($CDCl_3$, −20 °C): δ 13.8 (s, PBu_3), 24.3 (d, J_{PC} = 14.1 Hz, PBu_3), 24.7 (d, J_{PC} = 28.2 Hz, PBu_3), 25.3 (d, J_{PC} = 2.6 Hz, PBu_3), 66.0 (s, carbene OMe), 67.5 (s, aryl OMe), 113.4, 122.7, 124.6, 133.6, 135.1, 163.8 (6 s, aryl C), 229.3 (d, J_{PC} = 6.4 Hz, CO), 245.1 (d, J_{PC} = 29.5 Hz, CO), 301.4 (d, J_{PC} = 7.1 Hz, carbene C). ^{31}P NMR ($CDCl_3$): δ 7.74 (s and d, J_{PW} = 228 Hz). Anal. Calcd for $C_{23}H_{37}I_2O_4PW$ (846.2): C, 32.65; H, 4.41. Found: C, 33.11; H, 4.62.

Dibromotricarbonyl[methoxy(*p*-methoxyphenyl)carbene](tri-*n*-butylphosphine)tungsten(II) (12-A/12-B/12-B′). In an NMR tube, ca. 50 mg of **11** was dissolved in $CDCl_3$. $SnBr_4$ was added in excess, and the ^{1}H and ^{31}P NMR spectra were taken at room temperature. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and the IR spectrum recorded. IR (CH_2Cl_2): ν(CO) 2011 m sh, 1986 s, 1946 m, 1900 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.94 and 0.99 (2 t, J_{HH} = 7.0 Hz and J_{HH} = 7.1 Hz, 9H, PBu_3 of **B** and **A**), 1.25−1.67 (m, 12H, PBu_3 of **A** and **B**), 2.07−2.65 (m, 6H, PBu_3 of **A** and **B**), 3.86, 3.93, and 3.95 (3 s, 3H, aryl OMe of **A**, **B** and **B′**), 4.20 and 4.26 (2 s, 3H, carbene OMe of **A** and **B**) 6.91 ("d", J_{HH} = 8.8 Hz, 1H, aryl H of **A**), 7.06 ("d", J_{HH} = 9.0 Hz, 1H, aryl H of **B**), 7.61 ("d", J_{HH} = 9.0 Hz, 1H, aryl H of **B**), 7.79 ("d", J_{HH} = 8.8 Hz, 1H, aryl H of **A**). ^{31}P NMR ($CDCl_3$): δ 14.8 (s and d, J_{WP} = 243 Hz, **A**), 10.1 (s and d, J_{WP} = 223 Hz, **B**), 9.6 (s and d, J_{WP} = 223 Hz, **B′**). Molecular formula: $C_{24}H_{37}Br_2O_5PW$ (780.2).

Dibromotricarbonyl[methoxy(phenyl)carbene](tri-*n*-butylphosphine)tungsten(II) (14-A/14-B). The generation of **14-A/14-B** in $CDCl_3$ from ca. 50 mg of **13** and $SnBr_4$ and the spectroscopic investigations were carried out analogously to those of **12-A/12-B/12-B′**. The results were independent of whether the cis or the trans isomer of the starting complex was used. IR (CH_2Cl_2): ν(CO) 2026 w, 2016 w, 1987 m, 1940 s, 1902 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 and 0.99 (2 t, J_{HH} = 7.0 Hz and J_{HH} = 7.1 Hz, 9H, PBu_3 of **B** and **A**), 1.26−1.65 (m, 12H, PBu_3 of **A** and **B**), 2.07−2.66 (m, 6H, PBu_3 of **A** and **B**), 4.20 and 4.28 (2 s, 3H, carbene OMe of **A** and **B**), 7.38−7.44 (m, 1H, aryl H of **A** and **B**), 7.55−7.66 (m, 3H, aryl H of **A** and **B**), 7.75−7.83 (m, 1H, aryl H of **A** and **B**). Molecular formula: $C_{23}H_{35}Br_2O_4PW$ (750.2).

Dicarbonyldichloro[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](trimethylphosphine)molybdenum(II) (15a).

In an NMR tube, ca. 50 mg of **4a** was dissolved in CD_2Cl_2. PMe_3 (1 equiv) was added, and the ^1H and ^{31}P NMR spectra were taken at room temperature. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and the IR spectrum recorded. IR (CH_2Cl_2): ν(CO) 1981 m, 1907 vs cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.84 (d, $J_{PH} = 10.8$ Hz, 9H, PMe_3), 4.37 (s, 3H, carbene OMe), 4.67 (s, 3H, aryl OMe), 7.21−7.28 (m, 1H, aryl H), 7.34−7.37 (m, 1H, aryl H), 7.60−7.66 (m, 1H, aryl H), 7.80−7.84 (m, 1H, aryl H). ^{13}C NMR (CD_2Cl_2): δ 17.2 (d, $J_{PC} = 33.7$ Hz, PMe_3), 61.5 (s, carbene OMe), 63.4 (s, aryl OMe), 111.5, 123.1, 123.2, 132.5, 135.3, 162.8 (6 s, aryl C), 229.0 (d, $J_{PC} = 27.9$ Hz), 289.5 (d, $J_{PC} = 14.4$ Hz). Molecular formula: $C_{14}H_{19}Cl_2MoO_4P$ (449.1).

Dibromodicarbonyl[methoxy(*o*-methoxyphenyl)carbene-κ^2*C,O*](trimethylphosphine)molybdenum(II) (15b). The generation of **15b** in CD_2Cl_2 and the spectroscopic investigations were carried out analogously to those of **15a**. IR (CH_2Cl_2): ν(CO) 1981 m, 1910 vs cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.83 (d, $J_{PH} = 10.6$ Hz, 9H, PMe_3), 4.39 (s, 3H, carbene OMe), 4.77 (s, 3H, aryl OMe), 7.22−7.27 (m, 1H, aryl H), 7.35−7.38 (m, 1H, aryl H), 7.62−7.68 (m, 1H, aryl H), 7.83−7.86 (m, 1H, aryl H). ^{13}C NMR (CD_2Cl_2): δ 18.6 (d, $J_{PC} = 34.9$ Hz, PMe_3), 63.4 (s, carbene OMe), 65.8 (s, aryl OMe), 111.6, 123.0, 123.1, 131.6, 135.3, 163.0 (6 s, aryl C), 226.0 (d, $J_{PC} = 26.4$ Hz, 2CO), 289.5 (d, carbene C). Molecular formula: $C_{14}H_{19}Br_2MoO_4P$ (538.0).

Dibromotricarbonyl[methoxy(*o*-methoxyphenyl)carbene](triphenylphosphine)tungsten(II) (16). A 0.28 g (0.48 mmol) portion of **3b** was dissolved in 8 mL of CH_2Cl_2, and PPh_3 (0.13 g, 0.50 mmol) was added. The solution was stirred at room temperature. After a red precipitate had formed, the solution was cooled to −80 °C and the mixture was decanted. The red residue was dried in vacuo and washed twice with 10 mL of ether. Yield: 0.16 g (0.19 mmol, 40%) of a dark brick red powder. Mp: 135 °C dec. IR (CH_2Cl_2): ν(CO) 1964 s, 1870 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.87 (s, 3H, aryl OMe), 4.64 (s, 3H, carbene OMe), 6.96−7.00 (m, 1H, aryl H), 7.26−7.81 (m, 18H, aryl H and phenyl H). Due to poor solubility ^{13}C NMR and ^{31}P NMR could not be obtained. Anal. Calcd for $C_{30}H_{25}Br_2O_5PW$ (840.2): C, 42.89; H, 3.10. Found: C, 42.87; H, 3.15.

Dibromotricarbonyl[methoxy(*o*-methoxyphenyl)carbene](triphenylphosphine)molybdenum(II) (17). A 2.6 g (5.4 mmol) portion of **4b** was dissolved in 50 mL of CH_2Cl_2, and PPh_3 (2.8 g, 11 mmol) was added. After a short time, a red precipitate formed. After 30 min at room temperature the precipitate was collected either by filtering or by decanting the solution. After drying in vacuo, the red powder was analytically pure. Yield: 2.3 g, 3.0 mmol (56%). Mp: 117 °C dec. IR (CH_2Cl_2): ν(CO) 1976 vs, 1882 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.82 (s, 3H, aryl OMe), 4.64 (s, 3H, carbene OMe), 7.00−7.02 (m, 1H, aryl H), 7.28−7.45 (m, 16H, aryl H and phenyl H), 7.60−7.64 (m, 1H, aryl H), 7.78−7.82 (m, 1H, aryl H). ^{13}C NMR and ^{31}P NMR could not be recorded due to poor solubility. Anal. Calcd for $C_{30}H_{25}Br_2MoO_5P$ (752.3): C, 47.90; H, 3.35. Found: C, 47.66; H, 3.38.

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Supporting Information Available: IR and ^1H, ^{13}C, and ^{31}P NMR spectra of complexes **9c-A**/**9c-B**, **10b**, **10c**, **12**, **15a**, **15b**, **16**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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