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Synthesis of the first stable Fischer-type carbene metal complex with a C–O–P structural motive of the carbene ligand

Rainer Streubel *, Markus Hobbold, Siegfried Priemer

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, PO Box 3329, D-38023 Braunschweig, Germany

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Dedicated to Professor Othmar Stelzer on the occasion of his 60th birthday.

Abstract

Fischer-type (phenyl)carbene pentacarbonyltungsten complexes, which have an organo phosphorus moiety bonded to oxygen (**5**, **8**) or to nitrogen (**10a**,**b**), are synthesized by reaction of the O–Li and N–Li precursor carbene complexes with either bis(diisopropylamino)chlorophosphane (**5**) and/or [bis(trimethylsilyl)methylene]chlorophosphane (**8**, **10a**,**b**) via lithiumchloride elimination; whereas the bulky substituted complex **5** decomposed in solution under formation of bis(diisopropylamino)-chlorophosphaneoxide via an unknown reaction pathway, complex **8** was stable at ambient temperature; complexes **10a**,**b** slowly rearranged in solution to the 2*H*-azaphosphirene complex **11**; the complexes **8** and **10a**,**b** were unambiguously confirmed by NMR spectroscopy. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aminocarbene complexes; 2*H*-Azaphosphirene complexes; Tungsten; Rearrangements

1. Introduction

Since the discovery of stable carbene complexes by Fischer [1] alkoxycarbene metal complexes **I** have received widespread interest as powerful synthons in organic and organometallic synthesis [2]. Although the chemistry of carbene complexes that have a metal or a metalloid (Ti [3], B [4], Si [5]) bonded to the carbene oxygen atom **II** has been much less investigated, some useful applications have been described [6]. In contrast, no stable carbene metal complexes **III** that have an organo phosphorus moiety bonded to oxygen have been described, so far (Scheme 1). Reports showed that intermediately formed derivatives such as **1** [7] and **2** [8] undergo subsequent reactions like decomposition of **1** yielding a *trans*-bromocarbyne complex, carbon monoxide and triphenylphosphaneoxide [7] or, in the case of **2,** a dinuclear *Z*-1,2-diphosphite-alkene complex via a dimerization-like process and carbon monoxide [8]. Recently, we reported the first syntheses and structures of stable Fischer-type amino(methyl)- and amino(phenyl)carbene metal complexes having the bis(diisopropylamino)phosphanyl group bonded to nitrogen [9]. The observation that these complexes are perfectly stable at ambient temperature was a stimulus to attempt the synthesis of carbene complexes of the type **III** by using the bulkyness of the bis(diisopropylamino)phosphanyl group for kinetic stabilisation; our hope was to exclude subsequent reactions such as dimerization and/or coordination. Furthermore, we carried out a preliminary study on the influence of the coordination number of the phosphorus atom on the stability of such heteroatom-substituted carbene metal complexes (Scheme 1).

2. Results and discussion

Treatment of the acyl tungstate **3**, obtained by the reaction of tungsten hexacarbonyl with phenyllithium, [10] with the bis(diisopropylamino)chlorophosphane [11] **4** in diethyl ether at − 30°C gave the *O*-phosphanyl-substituted derivative **5** only as a reactive intermediate, which was detected by ^{31}P-NMR spectroscopy

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* Corresponding author. Tel.: + 49-531-3917350; fax: + 49-531-3915387.

E-mail address: r.streubel@tu-bs.de (R. Streubel).

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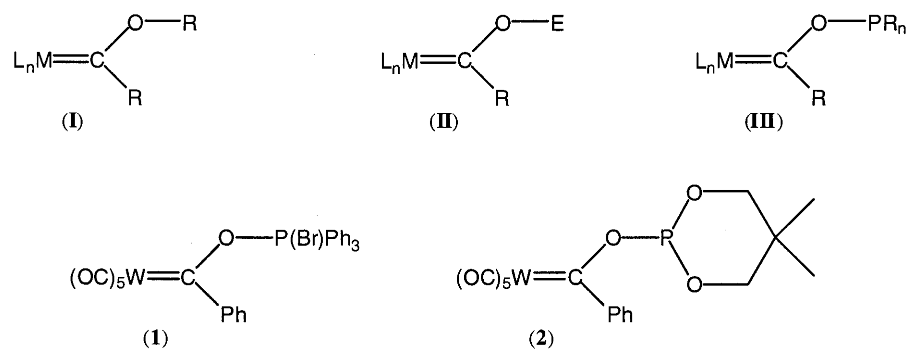
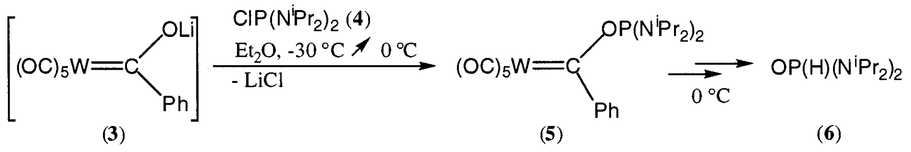


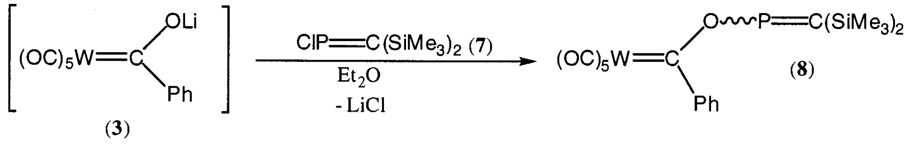
Scheme 1. Fischer-type carbene complexes with various C, O, E linkages ([M] = metal complex fragment, R denotes ubiquitous organic substituents, E = TiL$_n$, BR$_n$, SiR$_n$).

(**5a**: δ 152.9). This intermediate was unexpectedly unstable in solution at 0°C and decomposed to bis(diisopropylamino)phosphaneoxide [12] (**6**) (δ 9.6, ^{1}J(P, H) = 569.4 Hz) via an unknown reaction pathway (Scheme 2); the identity of phosphaneoxide **6** was established by using an authentic sample. So far, the fate of the complex fragment could not be determined (Scheme 2).

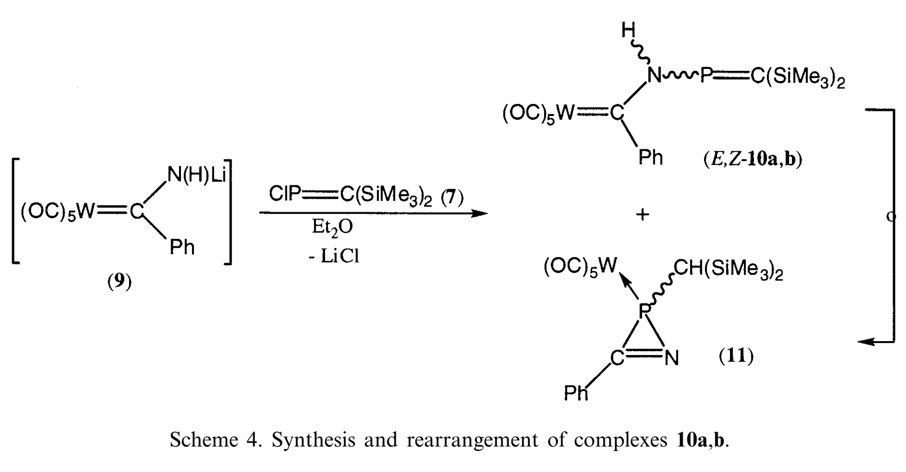
Treatment of the tungstate **3** with the [bis(trimethylsilyl)methylene]chlorophosphane [13] (**7**) in diethyl ether at − 30°C gave complex **8**, which was stable at ambient temperature (Scheme 3). A comparative study using the tungstate **9** [9a] and the methylene(chloro)phosphane **7** showed that the stability of the first products formed, complexes **10a**,**b**, and the general reaction course depended significantly on the sequence of reactants. If the tungstate **9** was added to the methylene(chloro)phosphane **7** complexes **10a**,**b** were formed as main products (1:1 mixture) and small quantities of the 2*H*-azaphosphirene complex **11** [14]; the latter was identified by adding an authentic sample (Scheme 4). Noteworthy is that a solution of the complexes **10a**,**b**



Scheme 2. Attempted synthesis of complex **5**.



Scheme 3. Synthesis of complex **8**.



Scheme 4. Synthesis and rearrangement of complexes **10a**,**b**.

showed a slow and clean conversion to the 2*H*-azaphosphirene complex **11**, thus confirming our earlier assumption [15] on the intermediacy of such complexes in 2*H*-azaphosphirene complex formation. The composition of complex **8** was confirmed by elemental analyses and mass spectrometry and the structural formulation of the complexes **8** and **10a**,**b** is based on their characteristic NMR spectral data in solution. The phosphorus nuclei of **8** and **10a**,**b** display resonances at $\delta = 348.1$ (**8**), 309.1 and 332.9 (**10a**,**b**), which are in the expected range of compounds with a low-coordinated phosphorus moiety, [16] thus excluding in both cases the η^2-coordination mode of the P=C unit to tungsten [17]. The conclusion that there is also no η^1 P,W-coordination in these cases derives from the absence of ^{183}W satellites in the ^{31}P-NMR spectra of complexes **8** and **10a**,**b** [17]. Proof for the structures of the complexes **8** and **10a**,**b** is given through the carbene atom resonances (**8**: $\delta = 320.6$, $^2J(\mathrm{P,C}) = 18.8$ Hz; **10a**,**b**: $\delta = 276.7$, $^2J(\mathrm{P,C}) = 1.6$ Hz and $\delta = 277.2$, $^2J(\mathrm{P,C}) = 1.4$ Hz) [18], which are in the typical range of related Fischer-type alkoxycarbene metal complexes. Also interesting is that the carbonyl carbon atoms of complexes **10a**,**b** showed no phosphorus–carbon couplings, whereas those of complex **8** did. Noteworthy is also that the complexes **10a**,**b** display an *E*,*Z*-isomerism at the C–N bond, thus representing the first examples of *E*,*Z*-isomers of *N*-phosphanyl aminocarbene complexes [9]; for related *N*-alkyl aminocarbene complexes such a phenomena has been reported earlier [18].

3. Experimental

3.1. General

All operations were carried out under an inert atmosphere of deoxygenated dry nitrogen. Solvents were dried according to standard procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81 MHz for 31P) using chloroform-d_6 and benzene-d_6 as solvents, the latter as internal standard; shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P); only coupling constant magnitudes are given. MS: Finnigan Mat 8430 (70 eV).Elemental analysis: Carlo Erba analytical gas chromatograph. IR: Biorad FTIR-165; selected data (ν(CO) bands) are given.

The following compounds were synthesized according to the literature: bis(diisopropylamino)chlorophosphane [11] (**4**), bis(diisopropylamino)phosphaneoxide [12] (**6**), [bis(trimethylsilyl)methylene]chlorophosphane [13] (**7**) and {[2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP]pentacarbonyl}tungsten(0)} (**11**)[14].

3.2. Attempted synthesis of {{*O*-[bis(diisopropylamino)phosphanyl]oxy(phenyl)-carbene}pentacarbonyltungsten(0)} (*5*)

A suspension of 0.40 g (1.5 mmol) of [bis(diisopropylamino)]chlorophosphane (**4**) in diethyl ether was added slowly to a stirred solution of freshly prepared **3** (reaction of 0.53 g (1 mmol) of $W(CO)_6$ with 0.75 ml (1.50 mmol) of a 1.6 m solution of phenyllithium in *n*-hexane) in 8 ml of diethyl ether at −15°C; afterwards the temperature was raised and the solution stirred for 3 h at 0°C. The ^{31}P-NMR spectrum (after 15 h) showed decomposition of the intermediately formed complex **5** to yield phosphaneoxide **6** as the main product.

3.3. Synthesis of {{*O*-[bis(trimethylsilyl)-methylenephosphanyl]oxy(phenyl)carbene}-pentacarbonyltungsten(0)} (*8*)

A solution of 0.36 g (1.5 mmol) of [bis(trimethylsilyl)methylene)chlorophosphane (**7**) in 1 ml of diethyl ether was added slowly to a stirred solution of freshly prepared **3** (reaction of 0.53 g (1.5 mmol) of $W(CO)_6$ with 0.60 ml of a 1.6 M solution of phenyllithium in *n*-hexane) at −30°C; afterwards the temperature was raised to ambient temperature and the solution stirred for 20 h. Evaporation of the solvent, filtration of lithiumchloride and concentration of the brown solution yielded complex **8** as a brownish solid (yield: 0.65 g (70%), m.p.: 83°C (dec.)). Elemental analysis: Anal. Found: C, 36.82; H, 3.63. Calc. For $C_{19}H_{23}O_6PSi_2W$ (618.42): C, 36.90; H 3.75%. IR (KBr): $\tilde{\nu} = 1915$ (vs), 1949 (s), 1980 (m), 2061 (m). MS [EI, 184 W, *m*/*z* (%)]: 618 [2, M^+], 590 [6, $M^+ - CO$], 562 [2, $M^+ - 2CO$], 534 [5, $M^+ - 3CO$], 506 [5, $M^+ - 4CO$], 478 [14, $M^+ - 5CO$], 401 [24, $M^+ - 5CO - Ph$], 373 [32, $M^+ - 5CO - PhCO$], 266 [30, $(C_{13}H_{23}PSi_2)^+$], 105 [23, $PhCO^+$], 77 [16, $C_6H_5^+$], 73 [100, $C_3H_9Si^+$]. ^{1}H-NMR ($CDCl_3$, 20°C): $\delta = 0.19$ (s, 9H, $Si(CH_3)_3$), 0.37 (d, $^4J(\mathrm{H,P}) = 2.5$ Hz, 9H, $Si(CH_3)_3$), 7.49 (m_c, 3H, *m*-, *p*-Ph), 7.83 (m_c, 2H, *o*-Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$, 20°C): $\delta = 1.5$ (d, $^3J(\mathrm{C,P}) = 14.4$ Hz, $Si(CH_3)_3$), 2.3 (d, $^3J(\mathrm{C,P}) = 2.5$ Hz, $Si(CH_3)_3$), 128.4 (s, Ph), 128.6 (s, Ph), 133.3 (s, Ph), 154.8 (d, $^3J(\mathrm{C,P}) = 3.9$ Hz, *i*-Ph), 173.9 (d, $^1J(\mathrm{C,P}) = 78.4$ Hz, C=P), 198.0 (d, $^4J(\mathrm{C,P}) = 8.3$ Hz, $^1J(\mathrm{C,W}) = 127.6$ Hz, *cis*-CO), 203.7 (d, $^2J(\mathrm{C,P}) = 2.4$ Hz, *trans*-CO), 320.6 (d, $^4J(\mathrm{C,P}) = 18.8$ Hz, *W*=CR_2). ^{31}P{^{1}H}-NMR ($CDCl_3$, 20°C): $\delta = 348.1$ (s).

3.4. Synthesis and rearrangement of a 1:1-mixture of *E*,*Z*-{{*N*-[bis(trimethylsilyl)methylenephosphanyl]-amino(phenyl)carbene}pentacarbonyltungsten(0)} (*10a*,*b*)

A solution of 0.36 g (1.5 mmol) of chlorophosphane **7** in 4 ml of diethyl ether was added slowly to a stirred solution of freshly prepared **9** (reaction of 0.65 g (1.5 mmol) of $\{(CO)_5W[C(NH_2)Ph]\}$ with 0.75 ml of a 1.6 M solution of methyllithium in *n*-hexane at 0°C, 10 ml of diethyl ether, 5 min) in 8 ml of diethyl ether at -30°C, afterwards the solution was allowed to warm up to 0°C and stirred for 0.5 h (yields of the crude products > 85%, dark yellow oil). Isolation of the complexes failed due to decomposition during low-temperature column chromatography (-30°C). Complexes **10a**,**b** rearranged slowly at ambient temperature to the 2*H*-azaphosphirene complex **11**.

Characterization of a 1:1 mixture of **10a**,**b**: $^{13}C\{^1H\}$-NMR (C_6D_6, 20°C): $\delta = 2.0$ (s, $Si(CH_3)_3$), 2.1 (s, $Si(CH_3)_3$), 2.3 (s br, $Si(CH_3)_3$), 122.1 (s br, Ph), 127.3 (s, Ph), 128.3 (s, Ph), 129.7 (s, Ph), 129.8 (s, Ph), 154.27 (d, $^3J(C, P) = 8.7$ Hz, *i*-Ph), 154.31 (d, $^3J(C, P) = 9.1$ Hz, *i*-Ph), 176.1 (d, $^1J(C, P) = 87.8$ Hz, P=C), 185.6 (d, $^1J(C, P) = 89.4$ Hz, P=C), 199.1 (s, $^1J(C, W) = 127.3$ Hz, *cis*-CO), 199.2 (s, $^1J(C, W) = 128.2$ Hz, *cis*-CO), 202.6 (s, *trans*-CO), 202.7 (s, *trans*-CO), 276.7 (d, $^2J(C, P) = 1.6$ Hz, W=CR_2), 277.2 (d, $^2J(C, P) = 1.4$ Hz, W=CR_2). $^{31}P\{^1H\}$-NMR (C_6D_6, 20°C): $\delta = 309.1$ (s, br), 332.9 (s, br).

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