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Formation of η^2-Ketene Rhenium(VII) Complex through the C,C-Coupling Reaction of Phosphonio Methylidyne Complexes with Carbon Monoxide

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A novel rhenium phosphonio methylidyne complex $[(^tBuN)_2Re(C\text{-}PPh_3)(S\text{-}^tBu)]$ (**3**) was obtained via one-pot transylidation reaction of $Re(N^tBu)_2Cl_3$ (**1**) with $[Ph_3P\text{-}CH_3][S\text{-}^tBu]$ (**2**) and 3 equiv of phosphorus ylide $Ph_3P{=}CH_2$. The η^2-ketene rhenium(VII) complex $[Re(N^tBu)_2\{\eta^2\text{-}(C,C)\text{-}O{=}C{-}C{=}PPh_3\}(S\text{-}^tBu)]$ (**4**) was formed through C,C-coupling reaction of complex **3** with CO. The structure of complex **4** was confirmed with X-ray analysis.

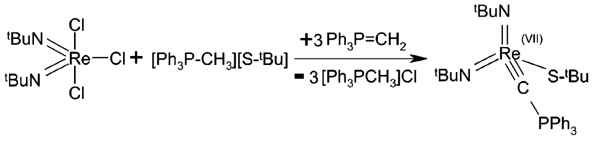
The synthesis of metal-carbyne complexes is always a hot topic in the research field of organometallic chemistry since the first synthesis of transition metal complexes with a formal metal−carbon triple bond reported by E. O. Fischer et al. in 1973[1] because of the great interest in the unusual properties of these compounds and their possible significance in organic synthesis and as intermediates in catalytic reactions. But only few complexes with a terminal $[M{\equiv}C\text{-}PR_3]$ function have been discovered so far.[2−5] Especially very few examples of phosphonio methylidyne complexes with d^0 electron configuration are known. Schmidbaur reported that the first complexes of d^0 electronic configuration $[X_2Ti(\mu\text{-}C\text{-}PR_3)_2TiX_2]$ contain the ligand $[R_3P\text{-}C]^{2-}$ in a bridging coordination mode in 1986.[6] They have interesting applications in C−C coupling reactions as a synthon for [C].[4−7] On the other side, interest in the catalytic metathesis of alkenes and alkynes was also the driving force for the development of high-valent (d^0) alkylidene and alkylidyne chemistry.[8]

Recently we have successfully used phosphorus ylides as a precursor for the formation of phosphonio methylidyne complexes of tungsten,[9] rhenium,[10] and niobium[11] with d^0 electron configuration. Complexes of this type have very reactive metal−carbon triple bonds, which react with nucleophilic reagents such as diphenyl ketene. The rhenium phosphonio methylidyne complex gives an allenylidene complex by reacting with diphenyl ketene through a Wittig reaction.[12]

The insertion reaction of small molecules such as CO into multiple metal−carbon bonds often is a decisive mechanism step in the organometallic catalytic cycle. Therefore such reactions always arouse research interest. There are many reports about this kind of research in the literature.[13−18]

Kreissl for the first time reported the synthesis of η^1- and η^2-ketenyl complexes of tungsten (Scheme. 1).[19] A (methyldiphenylphosphoranylidene)ketene complex of tungsten was obtained with carbon suboxide as a C_1 reagent.[20] Until now no report about the formation of a (phosphoranylidene)ketene complex of rhenium(VII) (d^0 configuration) has been found.

We now report the synthesis and characterization of a novel d^0 rhenium(VII) phosphonio methylidyne complex **3**. Reaction of complex **3** with CO gave the C−C-coupling product complex **4**. Complex **4** was structurally analyzed with X-ray diffraction.



1 **2** **3** (1)

Complex **3** was prepared through one-pot reaction of $Re(N^tBu)_2Cl_3$ (**1**), $(Ph_3PCH_3)(S\text{-}^tBu)$ (**2**), and $Ph_3P{=}CH_2$ ac-

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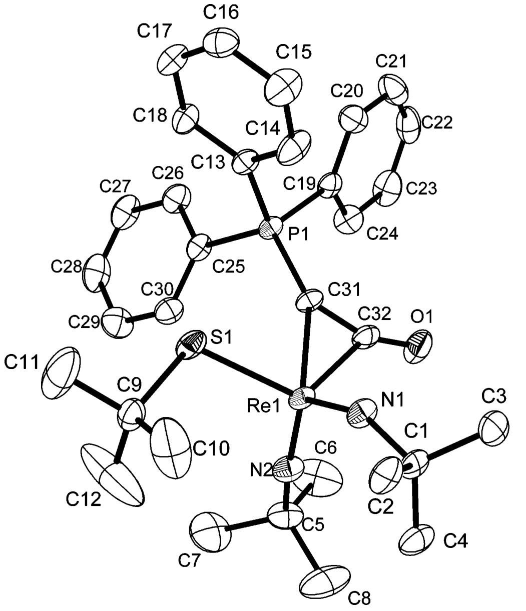
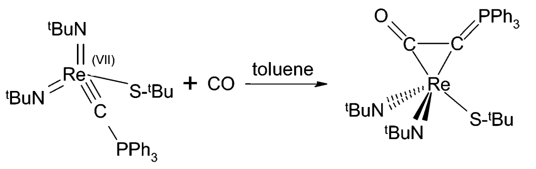


Figure 1. Molecular structure of **4**. Selected bond distances (pm) and angles (deg): Re1−N1 175.5(2), Re1−N2 172.7(3), Re1−C31 209.6(3), Re1−C32 217.1(3), Re1−S1 235.74(8), P1−C31 171.5(3), O1−C32 120.2(4), C31−C32 132.8(4), N1−Re1−N2 116.7(1), N1−Re1−C31 117.3(1), N2−Re1−C31 113.8(1), N1−Re1−C32 103.1(1), N2−Re1−C32 96.5(1), C31−Re1−C32 36.2(1), N1−Re1−S1 110.17(9), N2−Re1−S1 112.4(1), C31−Re1−S1 81.06(9), C32−Re1−S1 117.23(8).

cording to eq 1. Complex **3** was analytically and spectroscopically characterized. ^{31}P NMR spectra show one singlet at 10.0 ppm for the [Re≡CPPh$_3$] function. This is comparable with that of [Re(N^{t}Bu)$_2$(CPPh$_3$)(O^{t}Bu)] ($\delta_P = 6.8$ ppm)[21] and [Re(N^{t}Bu)$_2$(CPPh$_3$)(SR)] (R = adamantyl; $\delta_P = 10.8$ ppm).[12] The presence of a [Re≡CPPh$_3$] unit in complex **3** is also supported by the ^{13}C NMR spectrum, which contains a doublet at 256.8 ppm with a P−C coupling constant, ^1J(PC), of 10.1 Hz.

Treatment of a solution of complex **3** in toluene with carbon monoxide leads to a rapid change of color from red to yellow. Complex **4** was isolated as a yellow solid and characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy.



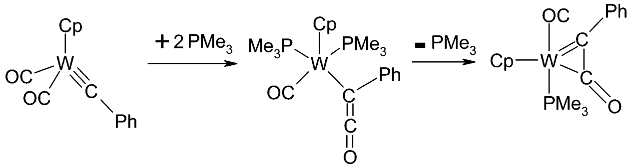
(2)

3 **4**

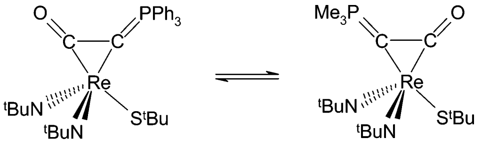
By recrystallization from pentane at 4 °C suitable single crystals of **4** as yellow prisms for X-ray diffraction analysis were obtained. The molecular geometry is shown in Figure 1 with selected bond distances and angles.

The geometry about the five-coordinate rhenium center is best described as a distorted tetrahedron with two imido groups, one ^{t}BuS-group, and one η^2-ketene ligand. The phosphacumulene ligand exists in η^2-ketene coordination. Bonds Re1−C31 und Re1−C32 are 209.6 and 217.1 pm, respectively. The distance C31−C32 of 132.8 pm is characteristic for η^2-coordination of a carbon−carbon double bond.[22] This value is comparable with that in carbonyl(η^5-cyclopentadienyl)(η^2-ketenyl)(trimethylphosphine)tungsten[19b] and dicarbonyl(η-cyclopentadienyl)(diphenylketene)manganese.[23] The P1−C13 distance (171.5 pm) is significant shorter than the other three P−C bond lengths. It may be considered that the P−C13 bond has some π-bond component according to one of the resonance forms of **4**. For the same reason Re−C31 (209.6 pm) is shorter than Re−C32 (217.1 pm). In contrast to the manganese complex, in this case space hindrance does not play an important role.

Scheme 1



Scheme 2



4a **4b**

In the IR spectrum of complex **4** two very strong CO bands at 1780 and 1815 cm^{-1} were recorded. A possible explanation is that the two isomers **4a** and **4b** of complex **4**, which can designated as in Scheme 2, in the solid state exist. In all of the NMR data only one sharp signal set was obtained. The transformation of these two isomers from one to another in solution is relatively fast on the NMR time scale. The crystal structure is identical with one of the conformations of complex **4** (isomer **4a**). Two doublets at 29.9 ppm with ^1J(PC) = 80.6 Hz and 173.1 ppm with ^2J(PC) = 6.8 Hz in the ^{13}C NMR spectrum correspond to the C31 and C32 atoms, respectively.

Complex **4** in the solid state is stable in air for more than one month without decomposition. In the case of the phosphonio methylidene complexes reported by Sundermeyer,[13] the C,C-coupling product with carbon monoxide as an intermediate was proposed but could not be isolated. A further rearrangement step gave rise to a *(C,O)*-coordinated phosphacumulene complex.

Experimental Section

General Procedures and Materials. All procedures were carried out under an argon atmosphere in freshly distilled anhydrous solvents. [Re(N^{t}Bu)$_2$Cl$_3$][24] was prepared by published procedures. NMR spectra were recorded on a Bruker AMX 400 spectrometer (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{31}P: 162.0 MHz). Elemental analyses were recorded on a Heraeus CHN-rapid. Single-crystal structures were determined with an ENRAF-Nonius CAD4.

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Preparation of Re(N^{t}Bu)$_2$(C-PPh$_3$)(S^{t}Bu) (3). A solution of [Ph$_3$P-CH$_3$][S-^{t}Bu] (**2**) (2.03 g, 5.52 mmol) in 10 mL of THF were dropwise added with stirring to a solution of 2.00 g (4.60 mmol) of Re(N^{t}Bu)$_2$Cl$_3$ (**1**) in 20 mL of THF at −78 °C. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm slowly to ambient temperature and stirred for 2 h. During this period the reaction solution turned dark red in color. Then a solution of 3.95 g (14.26 mmol) of Ph$_3$P=CH$_2$ in 30 mL of THF was added within 20 min to this mixture at −78 °C. A white flocculent precipitate was formed. The suspension was slowly heated to room temperature within 20 min and stirred for another 2 h, then filtered. After removal of the solvent at reduced pressure the red residue was extracted with 5 mL of toluene, and the addition of 30 mL of pentane caused the precipitation of a brown solid, which was separated by filtering and dried in vacuo. Yield: 2.26 g (71%) of **3**. Mp > 63 °C (dec). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 293 K): δ 1.46 (s, 18 H, NC(CH_3)$_3$), 1.74 (s, 9H, SC(CH_3)$_3$), 6.99−7.02 and 7.60−7.66 (m, 15H, P(C$_6$$H_5$)$_3$). ^{13}CNMR (C$_6D_6$, 100.6 MHz): δ 32.3 (s, NC(CH$_3$)$_3$), 35.4 (s, SC(CH$_3$)$_3$, 41.6 (s, SC(CH$_3$)$_3$), 68.0 (s, NC(CH$_3$)$_3$), 128.7 (d, ^3J(PC) = 11.9 Hz, PPh-C_{meta}), 130.0 (d, ^1J(PC) = 88.5 Hz, PPh-C_{ipso}), 131.6 (d, ^4J(PC) = 2.8 Hz, PPh-C_{para}), 133.5 (d, ^2J(PC) = 10.0 Hz, PPh-C_{ortho}), 256.8 (d, ^1J(PC) = 10.1 Hz, ReCP). ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ 10.0 (s, ReCP). Anal. Calcd for C$_{31}$H$_{42}$N$_2$PSRe (%): C 53.81, H 6.12, N 4.05, S 4.63. Found: C 53.69, H 5.89, N 3.88, S 4.73.

Preparation of [Re(N^{t}Bu)$_2${η^2-(C,C)-O=C−C=PPh$_3$}(S^{t}Bu)] (4). A 15 mL toluene solution of [Re(N^{t}Bu)$_2$(C-PPh$_3$)(S^{t}Bu)] (**3**) (200 mg, 0.29 mmol) was kept stirring under 1 bar of CO at room temperature. The reaction mixture was stirred for 2 h. During this period, the reaction mixture turned yellow in color. After removal of the solvent at reduced pressure the solid residue was extracted with pentane (30 mL) and diethyl ether (20 mL), respectively. Repeated recrystallization from pentane at 4 °C yielded yellow single crystals suitable for X-ray structure analysis. Yield: 375 mg (87%). Mp: 76 °C (dec). ^{1}H NMR (C$_6$D$_6$, 400.1 MHz): δ 1.52 (s, 18 H, NC(CH_3)$_3$), 1.60 (s, 9 H, SC(CH_3)$_3$), 6.99−7.01 and 7.75−7.81 (m, 15 H, P(C$_6$$H_5$)$_3$). ^{13}C NMR (C$_6D_6$, 100.6 MHz): δ 29.9 (d, ^1J(PC) = 80.6 Hz, CCP), 31.4 (s, NC(CH$_3$)$_3$), 35.5 (s, SC(CH$_3$)$_3$), 39.7 (s, SC(CH$_3$)$_3$), 69.7 (s, NC(CH$_3$)$_3$), 128.0 (d, ^1J(PC) = 90.7 Hz, Ph-C_{ipso}), 128.7 (d, ^3J(PC) = 12.5 Hz, Ph-C_{meta}), 132.2 (d, ^4J(PC) = 2.5 Hz, Ph-C_{para}), 134.1 (d, ^2J(PC) = 10.7 Hz, Ph-C_{ortho}), 173.1 (d, ^2J(PC) = 6.8 Hz, CCP). ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ 17.3 (s, ReCCP). Anal. Calcd for C$_{32}$H$_{42}$N$_2$OPSRe: C 53.38, H 5.88, N 3.89, S 4.45. Found: C 53.14, H 5.67, N 3.71, S 4.49. IR (Nujol): 1815 vs, 1780 vs (νCO).

Crystallographic data for 4: C$_{32}$H$_{42}$N$_2$OPSRe, M_r =719.93, crystal dimensions 0.50 × 0.40 × 0.30 mm, triclinic, space group $P\bar{1}$, a = 1005.3(10) pm, b = 1037.90(10) pm, c = 1663.00(10) pm, α = 88.524(11)°, β = 79.948(10)°, γ = 70.969(6)°, V =1580.8(2) Å^3, T = 193(2) K, Z = 2, D_c = 1.512 g cm^{-3}, μ = 3.986 mm^{-1}. A total of 11 743 reflections were collected, 5528 unique (R_{int} = 0.0247), $\theta_{\max}$ = 25.00°. R = 0.0220 ($I > 2\sigma(I)$), R_w = 0.0591 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

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Supporting Information Available: Tables containing full X-ray crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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