onance for the parent permethylated silane. This shift is attenuated as the site of the chloromethyl group becomes further removed from the specific silicon atom. Related substituent effects are observed in the ^{13}C NMR data; i.e., the methyl groups attached to the silicon containing the chloromethyl group, the α-position, are shielded by approximately 2.5 ppm, while those in the β-position are shifted to low frequency by 0.5 ppm. Such variations, while small, are regular and very useful for complete characterization of the new compounds.

Overall, this synthetic procedure provides an excellent route to a class of functional organosilicon compounds previously unavailable. The generality of this approach to a larger range of oligosilanes and related germyl-, stannyl-, and plumbylsilanes and poly(chloromethyl)silanes is under investigation, as is the chemical reactivity of the new system.

Acknowledgment. We acknowledge support of this research by DOD Grant DN-009, Defense Logistics Agency, Directorate of Stockpile Management, administered by the University of Texas at El Paso Institute of Manufacturing and Materials Management.

Registry No. $BrCH_2Cl$, 74-97-5; $ClSiMe_2SiMe_3$, 1560-28-7; $Cl(SiMe_2)_2SiMe_3$, 918-19-4; $Cl(SiMe_2)_3SiMe_3$, 51531-19-2; $ClSiMe(SiMe_3)_2$, 754-38-1; Cl_2SiMe_2, 75-78-5; $Cl(SiMe_2)_2Cl$, 4342-61-4; $ClCH_2SiMe_2SiMe_3$, 5181-46-4; $ClCH_2(SiMe_2)_2SiMe_3$, 15816-06-5; $ClCH_2SiMe(SiMe_3)_2$, 125091-02-3; $ClCH_2(SiMe_2)_3SiMe_3$, 127971-49-7; $(ClCH_2)_2SiMe_2$, 2917-46-6; $ClCH_2(SiMe_2)_2CH_2Cl$, 18139-99-6.

5-Metallo-2(3*H*)-furanones by Double Carbonylation of (σ-Allenyl)platinum and -palladium Compounds

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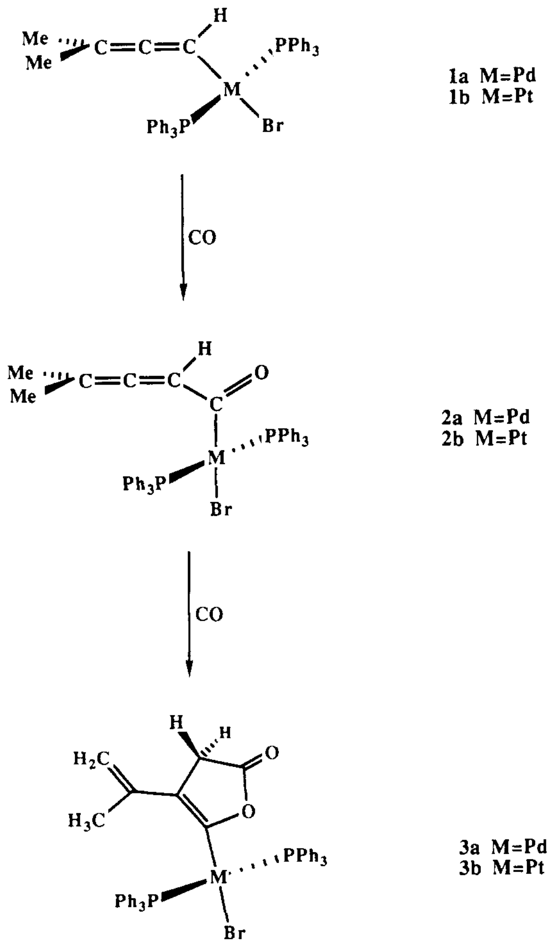
Summary: The reactions of bis(triphenylphosphine)(3-methylbuta-1,2-dien-1-yl)metal(II) bromide (M = Pd, Pt) with CO at 1.5 bar and 20 °C in benzene give the unexpected title compounds, which are formed by two successive insertions of carbon monoxide into metal–carbon bonds. An X-ray crystal structure study of the organoplatinum compound confirmed the proposed structure, featuring a square-planar bis(phosphine)organoplatinum(II) bromide in which the organic group is the unusual (nonconjugated) 2(3*H*)-furanon-5-yl moiety coordinated to platinum through an sp^2 carbon atom.

Studies aiming at the synthesis and isolation or observation of organometallic intermediates relevant to homogeneously catalyzed carbonylation reactions currently receive attention.[3] Apart from single migratory CO-insertion reactions quite a few double-carbonylation reactions have been reported.[4] During a study of palladium-catalyzed carbonylation reactions of allenic halides (alka-1,2-dienyl halides), we became interested in stoichiometric reactions of (σ-allenyl)palladium compounds with carbon monoxide in the absence of additional nucleophilic reagents. This interest stems from Tsuji's[5] and our[6] observation that alkoxycarbonylation of propargyl and allenyl compounds

Scheme I



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(1) Anorganisch Chemisch Laboratorium.

(2) Laboratorium voor Kristallografie.

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leads to unsaturated mono- as well as diesters. It was anticipated that reactions of allenylpalladium compounds such as **1a**[7] with CO would lead to carbonyl insertion products C=C=C-CO-PdL$_n$, which should subsequently be useful in mechanistic studies and might shed light on the nature of the complexes and sequence of events in the catalytic process. However, instead of the expected acylpalladium compound **2a** arising from single insertion of CO into the Pd-C bond of **1a**, the (2(3*H*)-furanon-5-yl)palladium complex **3a** was formed in a clean reaction. This novel compound arises via an as yet unprecedented sequence of two subsequent CO insertion reactions into metal carbon bonds, as will be elaborated below.

Stirring of a yellow solution of bis(triphenylphosphine)(3-methylbuta-1,2-dien-1-yl)palladium(II) bromide (**1a**) in C_6H_6 under an atmosphere of CO (1.5 bar) yielded an orange solution within 5 min. The product was identified as *trans*-bis(triphenylphosphine)(4-isopropenyl-2(3*H*)-furanon-5-yl)palladium(II) bromide (**3a**) on the basis of its ^{1}H, ^{13}C, and ^{31}P NMR, IR, and FD mass spectra obtained for the dissolved complex.[8] The bands in the IR spectrum at 1782 and 1609 cm^{-1} point to the presence of a vinyl ester, possibly in a five-membered ring. According to the mass data (including the isotopic pattern), the complex should contain the starting compound plus two molecules of CO. The ^{1}H NMR integral indicates the presence of two PPh_3 groups that should, according to the single ^{31}P NMR resonance, be oriented in mutually trans positions. ^{1}H NMR spectroscopy further shows resonances (slightly broadened singlets at 4.41 and 4.52 ppm (each 1 H) and a singlet at 2.27 ppm (3 H)) that are typical for an isopropenyl group and a triplet at 1.90 ppm (2 H) that is indicative of a methylene group with long-range coupling to two magnetically equivalent phosphorus nuclei. The chemical shift of the latter indicates that the methylene group will not be adjacent to oxygen as in α,β-unsaturated lactones but rather in an α-position relative to a vinyl and/or a carbonyl function. These inferences were corroborated by ^{13}C NMR spectroscopy and led us to assign **3a** as the most likely molecular structure of the new organopalladium(II) compound. Unfortunately, **3a** could not be crystallized; when it stands, the dissolved complex loses CO and a mixture of as yet unidentified products is formed.

In order to verify the structure of **3a**, the analogous Pt compound **3b**, which is expected to be kinetically more stable with respect to decomposition and deinsertion of CO, was synthesized. Thus, reaction of **1b** with CO as described for **1a** but during 20 h or at 20 bar of CO pressure and 50 °C in a stainless steel autoclave for 4 h gave, after evaporation of the solvent, yellow **3b** as an isolable compound in 72% yield. This new complex showed spectroscopic data comparable to those of **3a** and gave correct microanalytical data.[9]

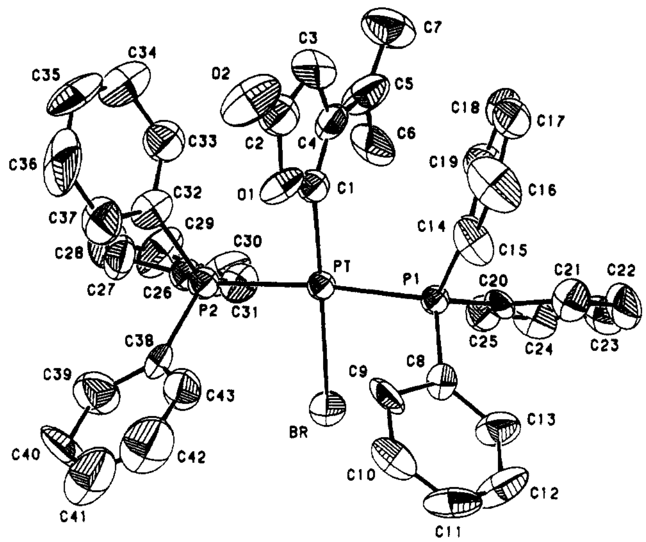
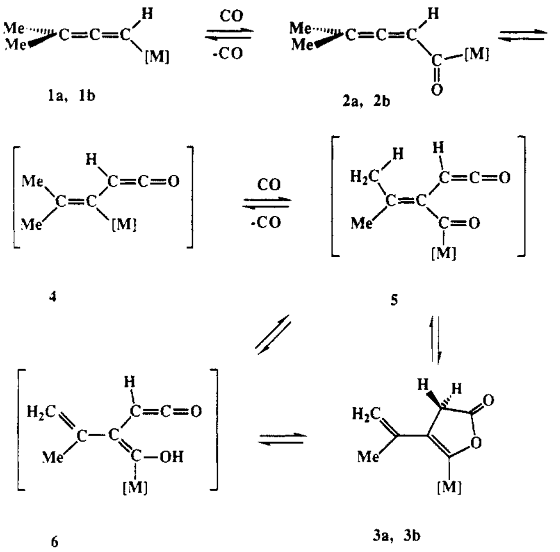


Figure 1. ORTEP representation of compound **3b**. Hydrogen atoms have been omitted for clarity. Important bond distances (Å) with standard deviations in parentheses: Pt-Br, 2.504 (2); Pt-P(1), 2.321 (4); Pt-P(2), 2.325 (4); Pt-C(1), 2.00 (1); O(1)-C(1), 1.42 (2); O(1)-C(2), 1.39 (2); O(2)-C(2), 1.22 (3); C(1)-C(4), 1.33 (2); C(2)-C(3), 1.46 (3); C(3)-C(4), 1.58 (3); C(4)-C(5), 1.46 (3); C(5)-C(6), 1.42 (3); C(5)-C(7), 1.37 (3). Important bond angles (deg): Br-Pt-P(1), 88.70 (10); Br-Pt-P(2), 88.28 (10); Br-Pt-C(1), 178.2 (4); P(1)-Pt-P(2), 172.5 (1); P(1)-Pt-C(1), 92.9 (4); P(2)-Pt-C(1), 90.2 (4); Pt-C(1)-O(1), 112 (1); Pt-C(1)-C(4), 134 (1); C(4)-C(5)-C(6), 117 (2); C(4)-C(5)-C(7), 120 (2); C(6)-C(5)-C(7), 123 (2).

Scheme II[a]



[a] [M] = $Pd(PPh_3)_2Br$ or $Pt(PPh_3)_2Br$.

Single crystals of **3b** could be obtained by allowing slow diffusion of hexane into a benzene solution of **3b** at ambient temperature. An X-ray structure determination provided confirmation of the proposed structure, which

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(8) Selected data for **3a**: ^{1}H NMR (CD_2Cl_2, 250 MHz) δ 1.90 (t, ^5J(P,H) = 6.7 Hz, 2H, $-CH_2-$), 2.27 (s, 3 H, CH_3), 4.41 (s, 1 H, $=CH_2$), 4.52 (s, 1 H, $=CH_2$), 7.3 (m, 18 H, meta and para Ph), 7.7 (m, 12 H, ortho Ph); ^{31}P NMR (C_6D_6, 100 MHz) δ 20.99 (s); ^{13}C NMR (CD_2Cl_2, 250 MHz) δ 22.55 (s, CH_3), 33.63 (s, $-CH_2-$), 108.06 (s, $=CH_2$), 123.29 (t, ^3J(P,C) = 5.3 Hz, *C*—C—Pd), 128.37 (t, ^3J(P,C) = 5.1 Hz, Ph C_3), 130.90 (s, Ph C_4), 131.18 (t, ^1J(P,C) = 23.8 Hz, Ph C_1), 135.04 (t, ^2J(P,C) = 6.2 Hz, Ph C_2), 138.07 (s, Me—*C*), 170.88 (t, ^2J(P,C) = 7.5 Hz, C=*C*—Pd), 176.23 (s, O—*C*=O); IR (KBr, cm^{-1}) ν(O—C=O) 1782 (vs), ν(C=C) 1609 (m); FD mass found m/z = 834, calcd $M^{\bullet +}$ 834.

(9) Selected data for **3b**: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 1.89 (m, ^5J(P,H) = 2.8 Hz, ^4J(Pt,H) = 17.1 Hz, 2 H, $-CH_2-$), 2.16 (s, 3 H, CH_3), 4.45 (s, 1 H, $=CH_2$), 4.48 (s, 1 H, $=CH_2$), 7.3 (m, 18 H, meta and para Ph), 7.7 (m, 12 H, ortho Ph); ^{31}P NMR (C_6D_6, 100 MHz) δ 19.11 (s, J(Pt,P) = 2883 Hz); ^{13}C NMR (CD_2Cl_2, 200 MHz) δ 22.91 (s, CH_3), 34.05 (s, $-CH_2-$), 107.84 (s, $=CH_2$), 120.14 (m, *C*—C—Pt), 128.33 (t, ^3J(P,C) = 5.4 Hz, Ph C_3), 130.27 (m, ^2J(Pt,C) = 28.7 Hz, ^1J(P,C) = 29.7 Hz, Ph C_1), 131.09 (s, Ph C_4), 135.21 (m, ^2J(P,C) = 6.1 Hz, Ph C_2), 138.42 (m, Me—*C*), 177.06 (s, O—*C*=O); IR (KBr, cm^{-1}) 1785 (vs) ν(O—C=O), 1608 (m) ν(C=C); FD-mass found m/z = 922, calcd $M^{\bullet +}$ 922. Anal. Calcd for $C_{43}H_{37}O_2P_2PtBr{\cdot}C_6H_6$: C, 58.81; H, 4.33; O, 3.19; P, 6.19. Found: C, 59.02; H, 4.43; O, 2.92; P, 6.28.

is shown as an ORTEP plot in Figure 1.[10] The platinum atom is surrounded by a bromine, two phosphorus, and one carbon atom in a slightly distorted square planar geometry. The phosphorus atoms occupy mutual trans positions. The carbon fragment can be identified as a substituted 2(3*H*)-furanone, bearing an iso-C_3 fragment at the 4-position and a platinum substituent at the 5-position. A rationalization of the reaction sequence for the formation of **3** is shown in Scheme II.

The first step in the formation of **3** is CO insertion into the metal–carbon bond of **1**, which results in the acyl complex **2**. Compound **2b** has indeed been isolated from reaction of **1b** with CO (1.5 bar during 14 h). The acylplatinum compound **2b** has been fully characterized[15] and was shown in a separate experiment to react further with CO to give **3b**. The existence of acylpalladium compound **2a** has been confirmed by low-temperature ^{1}H NMR and IR experiments. Under an atmosphere of CO at temperatures higher than 0 °C this complex reacts further to give **3a**.

The next step in the reaction sequence is a 1,3-metal shift resulting in the vinylketene intermediate **4**, followed by a second CO insertion into the new metal–carbon bond to give the metallo-α-acylketene compound **5** (not observed). The occurrence of the ketene intermediate **4** is indicated by the observation of a strong absorption at 2092 cm^{-1} in the IR spectrum during the conversion of **1** or **2** into **3**.[16] The last step may consist of ring closure concomitant with a 1,4-H shift, or alternatively a metal-promoted enolization via **6** may occur. Intermediate **6** has been neither observed nor isolated, but an α-acylketene is known to give a butenolide after enolization and cyclization.[17] The latter process would in our case involve a 1,5-hydrogen shift of a hydrogen atom from either of the two methyl groups to the oxygen atom of the metalloacyl group to give **6**, followed by normal addition of the enolic OH function to the ketene moiety.

Currently, investigations on the reactivity of the metallofuranone complexes toward small molecules and organometallic reagents with the aim of catalytic synthesis of derivatized butenolides are in progress.

Acknowledgment. We thank Prof. K. Vrieze for his interest.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal data and data collection and refinement parameters, atomic coordinates, thermal parameters, and bond distances and angles (12 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for compound **3b**: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.613$ (1) Å, $b = 34.694$ (4) Å, $c = 11.007$ (2) Å, $\beta = 104.07$ (1)°, $V = 4031.7$ Å^3, μ(Mo Kα) = 43.19 cm^{-1}, $d_{calc} = 1.43$ g cm^{-3}. Crystal dimensions were 0.25 × 0.50 × 0.50 mm. A total of 7673 intensities were measured on a Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.710\,69$ Å) radiation ($1.1 \le \theta \le 25°$; h −13 to 13, k 0–41, l 0–13). Of these, 2486 were below the $2.5\sigma(I)$ level and were treated as unobserved. The structure was solved by means of the heavy-atom method. Refinement was carried out by means of anisotropic block-diagonal least-squares calculations. The hydrogen atoms were introduced at their calculated positions and not refined. An empirical absorption correction (DIFABS) has been applied.[11] The weighting scheme $w = 1/(50 + F_o)$ has been employed, and the anomalous dispersions of Pt, Br, and P have been taken into account. The final R value was 0.053 ($R_w = 0.089$). The calculations were carried out with XTAL 2.4.[12] The scattering factors and the dispersion correction factors were taken from the literature.[13,14]

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(13) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(15) Selected data for **2b**: ^{1}H NMR (C_6D_6, 100 MHz) δ 1.56 (d, ^5J(H,H) = 2.8 Hz, 6 H, 2 CH_3), 5.23 (m, ^3J(Pt,H) = 37 Hz, 1 H, =C=CH–), 7.00 (m, 18 H, meta and para Ph), 7.90 (m, 12 H, ortho Ph); ^{31}P NMR (C_6D_6, 100 MHz) δ 19.51 (s, J(Pt,P) = 3071 Hz); IR (KBr, cm^{-1}) ν(C=O) 1620 (vs), ν(C=C=C) 1940 (w); FD-mass found m/z = 895, calcd M$^{\bullet+}$ 895.

(16) Alternatively, a σ- to π-allyl conversion followed by carbonylation of the (π-allyl)palladium species may be involved. The intermediate π-allylic ligand would be intriguing because of the unsaturation at both terminal allyl carbon atoms. We thank one of the reviewers for drawing our attention to this point.

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Synthesis of the First Stable 1,2-Silathietane

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Summary: Sulfur reacts with 1,1-di-*tert*-butyl-2,3-dimethylsilirane (**1**) to produce the first isolable silthietane, 1,1-di-*tert*-butyl-3,4-dimethyl-1,2-silathietane (**2**), and 1,1-di-*tert*-butyl-3,4-dimethyl-1-sila-2,3-dithiacyclopentane (**3**) in 60% and 19% yields, respectively. Pyrolysis (200 °C) of **2** generates 1,1,3,3-tetra-*tert*-butyl-2,4-dithiadisilacyclobutane (**4**) and 1,1,3,3-tetra-*tert*-butyl-5,6-dimethyl-2,4-dithia-1,3-disilacyclohexane (**5**). **4** is formally the dimer of the reactive intermediate di-*tert*-butylsilathione, *t*-Bu_2Si=S, and **5** is the product of insertion of the silathione fragment into **2**. When **1** is heated in the presence of hexamethylcyclotrisiloxane, 1,1-di-*tert*-butyl-3,3,5,5,7,7-hexamethyl-2,4,6-trioxa-1,3,5,7-tetrasila-8-thiacyclooctane (**6**) is formed. Sulfur insertion into **1** to produce **2** is stepwise, as is the cleavage of **2**.

1,2-Silathietanes have been postulated as reactive intermediates in the reaction of thio ketones with silenes at high temperatures en route to silathiones.[1] However, characterization of any member of this ring system has, until now, proven elusive. Insertion of sulfur into cyclic carbosilanes is a well-known and useful method of preparing unusual sulfur-containing heterocycles.[2] However, in the case of siliranes with small substituents on silicon, the reaction with sulfur cannot be limited to single-atom insertion and thus is not a viable route to stable 1,2-silathietanes.[3] We have found that by placing *tert*-butyl

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