Stable η^1-Alkynyl−μ,η^1:η^2-Alkenyl Complexes from the Reaction of Terminal Alkynes with Encumbered Dinuclear Platinum Compounds and Their Formyl, Methoxycarbonyl, and Hydride Derivatives

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Summary: The stepwise reaction of terminal alkynes with [(OC)Pt(μ-PBu$^t_2$)$_2$Pt(H)(PBu$^t_2$H)]OTf yields intermediate η^1-alkynyl−hydride-bridged complexes, and then stable η^1-alkynyl/alkenyl-bridged derivatives containing an electrophilic carbonyl ligand. The latter is attacked by nucleophiles (H^- and MeO^-) to give a rare platinum formyl species, which is slowly converted into a stable hydride or a stable methoxycarbonyl complex.

Linear oligomerizations of terminal alkynes to give enynes or butatrienes are catalyzed by several mononuclear metal complexes.[1−3] The C−H bond is generally activated through oxidative addition[2j,k,m] or σ-bond metathesis[1a,b,2c,l] to give an alkynyl−hydride (or vinylidene) or an alkynyl complex, respectively. This step is followed by the formation of a C−C bond through the insertion of a second alkyne into the metal−alkynyl or −vinylidene bond[1a,b,2a−f,l−n] or, more rarely and after alkyne insertion into the metal−hydride bond, by alkynyl−vinyl coupling.[2k] Further insertions of alkyne molecules before the product-forming σ-bond metathesis (or reductive elimination) step may elongate the oligomer chain.[1b]

Polynuclear systems may offer alternative coordination modes and reaction paths to the various functionalities,[4] therefore providing new opportunities to catalyst design. Indeed, most of the aforementioned *single* steps have their well-established analogues in di- or polynuclear complexes. However, up to now the observation of a *sequence* of such steps, gathering fragments from two or more 1-alkyne molecules on the same polynuclear framework, is sporadic. Relevant examples are the isolation of vinyl−alkynyl−vinylidene,[5] vinyl−,[6] vinylidene−,[7] or alkynyl−alkyne,[8] bis(alkynyl)[8,9] and ene−diyne[9b] complexes, and the suggested intermediacy of alkynyl−vinylidene or −allenylidene derivatives[10] followed by CC coupling and the formation of dinuclear metallacycles. To the best of our knowledge, the completion of an entire catalytic cycle has been demonstrated only once.[11]

Herein is described the stepwise reactions of 1-alkynes with [(OC)Pt(μ-PBu$^t_2$)$_2$Pt(H)(PBu$^t_2$H)]OTf (**1**; Tf = CF_3SO_2),[12] which eventually afford new η^1-alkynyl−μ,η^1:η^2-alkenyl derivatives, as well as some interesting aspects of their reactivity. Complex **1** reacts reversibly with an equimolar amount of PhCCH or with a 3/1 excess of Bu^{t}CCH to give the hydride-bridged [(η^1-RCC)(Bu$^t_2$HP)Pt(μ-PBu$^t_2$)(μ-H)Pt(CO)(PBu$^t_2$H)]OTf, (**2a**, R = Ph; **2b**, R = Bu^t; Scheme 1).[13] The reactions proceed through the formation of a P−H bond by coupling of the hydride and the adjacent phosphide[14] and the oxidative addition

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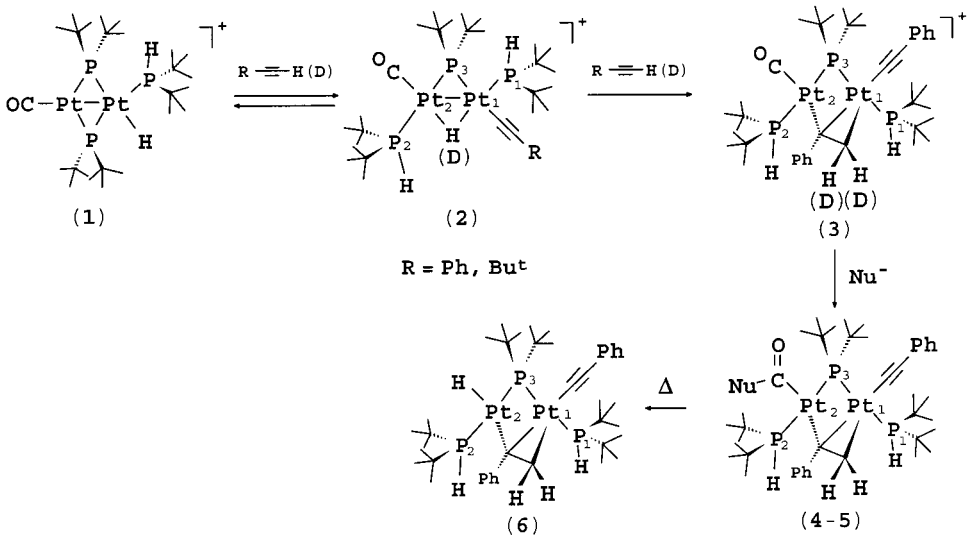
Scheme 1



of the C−H bond of the alkyne. This is clearly demonstrated by the selective formation of [(η^1-PhCC)(Bu^t_2HP)Pt(μ-PBu^t_2)(μ-D)Pt(CO)(PBu^t_2H)]OTf, (**2a-D**) in the reaction of **1** with PhCCD.[15]

While **2b** is stable indefinitely in the presence of an excess of *tert*-butylacetylene, **2a**, which decomposes slowly to unidentified products on standing in solution, reacts rapidly with an excess of phenylacetylene. In this reaction the second alkyne unit is inserted into the Pt_1-Pt_2(μ-H) moiety to give the alkenyl-bridged [(η^1-PhCC)-(Bu^t_2HP)Pt(μ-PBu^t_2)($\mu,\eta^1{:}\eta^2$-C(Ph)=CH_2)Pt(CO)(PBu^t_2H)]-OTf (**3**) in nearly quantitative yield. Complex **3** was characterized by elemental and spectroscopic analyses[16] and by single-crystal X-ray diffraction.[17] The structure of cation $\mathbf{3}^+$ is shown in Figure 1 together with some relevant geometric parameters. Pt and P atoms, C(3), and the carbonyl and phenylethynyl ligands approximately lie on a plane (maximum deviation 0.16 Å); the phenyl group of the phenylethenyl ligand is perpendicular (87°) to the same plane.

Cation $\mathbf{3}^+$ contains a single phosphide ligand bridging two nonbonded platinum centers (Pt(1)···Pt(2) = 3.567-

(13) An acetone solution of **1** yields rapidly and quantitatively **2a** or **2b** after the addition of an equimolar amount of PhCCH at −60 °C or a 3-fold excess of *t*-BuCCH at room temperature. When it is warmed to room temperature, **2a** decomposes to a mixture of products, while **2b** can be isolated as a stable, pale yellow solid (53%) by adding *n*-hexane. Anal. Calcd for $C_{32}H_{66}F_3O_4P_3Pt_2S$: C, 35.3; H, 6.13. Found: C, 35.6; H, 6.17. Complex **2a*** was prepared as **2a** by starting from [($O^{13}C$)Pt(μ-PBu^t_2)$_2$Pt(H)(PBu^t_2H)]OTf (**1***). In this and in all following references, # denotes values of J_{XPt} from ^{195}Pt satellites.[12,14] **2a**: ^{1}H NMR (acetone-d_6, 213 K) δ (ppm)# −5.1 (ddd, J_{HP} = 11, 13, 52, $^1J_{HPt}$ = 402, 591 Hz, 1 H, μ-H), 1.2−1.8 (m, 54 H, CCH_3), 5.5 (d, $^1J_{HP}$ = 374 Hz, 1 H, P*H*), 6.1 (dd, $^1J_{HP}$ = 376, $^3J_{HP}$ = 12, $^2J_{HPt}$ = 44 Hz, 1 H, P*H*), 7.2−7.6 (m, 5 H, C_6H_5); ^{31}P{^{1}H} NMR (acetone-d_6, 213 K)# δ (ppm) 23.9 (s, $^1J_{P_1Pt_1}$ = 3782, $^2J_{P_1Pt_2}$ = 373 Hz, P_1), 39.4 (d, $^2J_{P_2P_3}$ = 150, $^1J_{P_2Pt_2}$ = 1970 Hz, P_2), 212.3 (d, $^2J_{P_2P_3}$ = 150, $^1J_{P_3Pt_1}$ = 1963, $^1J_{P_3Pt_2}$ = 1260 Hz, P_3), further splitting in the H-coupled spectrum for the signals at 23.9 (d, $^1J_{HP}$ = ca. 375 Hz) and 39.4 (dd, $^1J_{HP}$ = ca. 375); ^{195}Pt{^{1}H} NMR (acetone-d_6, 213 K) δ (ppm) −5559 (dd, $^1J_{Pt_1P_1}$ = 3782, $^1J_{Pt_1P_3}$ = 1963 Hz, Pt_1), −5677 (ddd, $^1J_{Pt_2P_2}$ = 1970, $^1J_{Pt_2P_2}$ = 1260, $^2J_{Pt_2P_1}$ = 373 Hz, Pt_2); IR ($CHCl_3$) 2097 s (ν_{CO}) cm^{-1}. **2a***: ^{31}P{^{1}H} and ^{1}H NMR spectra as for **2a**; ^{195}Pt{^{1}H} NMR (acetone-d_6, 213 K) δ (ppm) −5559 (dd as for **2a**, Pt_1), −5677 (dddd, J_{PtP} as for **2a** and $^1J_{Pt_3C}$ = 1780 Hz, Pt_2); ^{13}C{^{1}H} NMR (acetone-d_6, 213 K) δ (ppm)# 28.1−33.5 (m, CCH_3), 126.5−132.9 (all s, Ph), 175.6 (strong s, $^1J_{CPt}$ = 1780 Hz, *C*O). **2b**: ^{1}H NMR (acetone-d_6, 293 K) δ (ppm)# −5.1 (ddd, J_{HP} = 11, 12, 52, $^1J_{HPt}$ = 406, 600 Hz, 1 H, μ-H), 1.2 (s, 9 H, CC−CCH_3), 1.4−1.7 (three d, $^3J_{HP}$ = 16 Hz, 54 H, PCCH_3), 5.56 (d, $^1J_{HP}$ = 370 Hz, 1 H, P*H*), 6.0 (dd, $^1J_{HP}$ = 367, $^3J_{HP}$ = 14, $^2J_{HPt}$ = 42 Hz, 1 H, P*H*); ^{31}P{^{1}H} NMR (acetone-d_6, 293 K) δ (ppm)# 24.7 (s, $^1J_{P_1Pt_1}$ = 3838, $^2J_{P_1Pt_2}$ = 382 Hz, P_1), 40.7 (d, $^2J_{P_2P_3}$ = 150, $^1J_{P_2Pt_2}$ = 1966 Hz, P_2), 211.2 (d, $^2J_{P_2P3}$ = 150, $^1J_{P_3Pt_1}$ = 1934, $^1J_{P_3Pt_2}$ = 1263 Hz, P_3); ^{195}Pt{^{1}H} NMR (acetone-d_6, 293 K) δ (ppm) −5514 (dd, $^1J_{Pt_1P_1}$ = 3838, $^1J_{Pt_1P_3}$ = 1934 Hz, Pt_1), −5623 (ddd, $^1J_{Pt_2P_2}$ = 1966, $^1J_{Pt_2P_3}$ = 1263, $^2J_{Pt_2P_1}$ = 382 Hz, Pt_2); IR ($CHCl_3$) 2092 s (ν_{CO}) cm^{-1}.

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(15) Complex **2a-D** was prepared as for **2a**, starting from **1** and PhCCD. **2a-D**: ^{1}H NMR (acetone-d_6, 213 K) as for **2a**, except the hydride signal is missing at −5.1 ppm; ^{31}P{^{1}H} and ^{31}P NMR (acetone-d_6, 213 K) as for **2a**; ^{195}Pt{^{1}H} NMR (acetone-d_6, 213 K) δ (ppm) −5559 (ddt, $^1J_{Pt_1P_1}$ and $^1J_{Pt_1P_3}$ as for **2a**, $^1J_{Pt_1D}$ = 62 Hz, Pt_1), −5677 (dddt, $^1J_{Pt_2P_2}$, $^1J_{Pt_2P_3}$ and $^2J_{Pt_2P_1}$ as for **2a**, $^1J_{Pt_2D}$ = 91 Hz, Pt_2).

(16) Complex **3** was isolated as a stable, colorless solid (65% yield) by reacting an acetone solution of **1** with a 2.5-fold excess of PhCCH at −30 °C. Anal. Calcd for $C_{41}H_{68}F_3O_4P_3Pt_2S$: C, 41.1; H, 5.72. Found: C, 40.8; H, 5.76. Complex **3*** was prepared analogously, by starting from **1***. **3-D_2** was prepared by starting from **1** and PhCCD. **3**: ^{1}H NMR (CD_2Cl_2, 293 K) δ (ppm)# 1.00, 1.31, 1.49, 1.59, 1.69, 1.185 (all d, $^3J_{HP}$ = 14.5−15.7 Hz, 54 H, CH_3), 3.35 (d, $^1J_{HP}$ = 374, $^2J_{HPt}$ = 22 Hz, 1 H, P*H*), 4.54 (d, $^1J_{HP}$ = 340, $^2J_{HPt}$ = 20 Hz, 1 H, P*H*), 4.53 (m, $^2J_{HPt}$ = 17.3, 61.6 Hz, 1 H, PhCC(*H*)H), 5.02 (m, $^2J_{HPt}$ = 47.5 Hz, 1 H, PhCC(H)*H*), 7.25, 7.50, 7.89 (all m, 10 H, Ph); ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K) δ (ppm)# −52.0 (dd, $^2J_{P_3P_1}$ = 199, $^2J_{P_3P_2}$ = 323, $^1J_{P_3Pt_1}$ = 1630, $^1J_{P_3Pt_2}$ = 2046 Hz, P_3), 43.6 (dd, $^2J_{P_2P_3}$ = 323, $^3J_{P_2P_1}$ = 7.2, $^1J_{P_2Pt_2}$ = 1875 Hz, P_2), 72.7 (dd, $^2J_{P_1P_3}$ = 199, $^3J_{P_1P_2}$ = 7.2, $^1J_{P_1Pt_1}$ = 1797 Hz, P_1), further splitting in the H-coupled spectrum for the signals at 43.6 (ddd, $^1J_{P2H}$ = 340 Hz) and at 72.7 (ddd, $^1J_{P_1H}$ = 374 Hz); ^{195}Pt{^{1}H} NMR (CD_2Cl_2, 293 K) δ (ppm) −4167 (dd, $^1J_{Pt_2P_3}$ = 2046, $^1J_{Pt_2P_2}$ = 1875 Hz, Pt_2), −4406 (dd, $^1J_{Pt_1P_3}$ = 1630, $^1J_{Pt_1P_1}$ = 797 Hz, Pt_1); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K) δ (ppm)# 30.5−31.5, 32.7, 33.9 (all br s, PCCH_3), 33.3, 35.2, 35.8, 36.8, (w d, $^1J_{CP}$ = 20 Hz, PCCH_3), 38.8, 38.9 (w m, PCCH_3), 87.1 (w s, J_{CPt} = 770 Hz, PhC*C*), 88.2 (w s, J_{CPt} = 112, 77 Hz, PhCCCH_2 (t in the proton-coupled spectrum, $^1J_{CH}$ = 158 Hz)), 117.6 (w s, J_{CPt} = 403 Hz, Ph*C*C), 121.3 (q, $^1J_{CF}$ = 320 Hz, *C*F_3) 126.7, 128.4, 128.9, 130.1, 130.3 (all s, Ph), 144.5 (w s, J_{CPt} = 22 Hz, PhC*C*H_2), 181.9 (w s, J_{CPt} = 1070 Hz, *C*O); IR ($CHCl_3$) 2116 w (ν_{CC}), 2086 s (ν_{CO}) cm^{-1}. **3***: same signals as complex **3**, except further splitting for the signal at −4167 ppm ($^1J_{Pt_2C}$ = 1070 Hz) in the ^{195}Pt{^{1}H} NMR, the intensity of the signal at 181.9 ppm (strong s) in the ^{13}C{^{1}H} NMR, and a shift in the ν_{CO} absorption (2036 cm^{-1}) in the IR spectrum. **3-D_2**: same signals as for **3**, except those missing at 4.53 and 5.02 ppm in the ^{1}H NMR.

(17) Crystal structure analysis of **3**·OC_4H_8: $C_{46}H_{76}F_3O_5P_3Pt_2S$, M_r = 1281.22, triclinic, space group $P\bar{1}$, a = 9.184(1) Å, b = 11.799(2) Å, c = 25.968(5) Å, α = 88.69(1)°, β = 89.73(1)°, γ = 72.54(1)°, V = 2683.6(7) Å^3, Z = 2, F(000) = 1272, D_c = 1.586 Mg m^{-3}, T = 293 K, crystal dimensions 0.76 × 0.48 × 0.09 mm^3. Intensity data were collected on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); 5070 nonzero (2σ) out of 6945 independent reflections were collected (R_{int} = 0.0655) with 2.32 ≤ θ ≤ 22.50°. The structure was solved by standard Patterson and Fourier methods (SHELX-97) and refined by least squares on F^2 (SHELXTL). R1 = 0.0814, wR2 = 0.1868; 463 parameters were refined. Pt, S, P, and F are anisotropic, O and C are generally anisotropic, except for some *tert*-butyl groups and those of the solvent thf molecule, and H is isotropic. The final difference Fourier map showed residuals of electron density high up to 3.166 e Å^{-3}. This residuals may be due to the disorder in *tert*-butyl groups or, possibly, to an incomplete absorption correction.

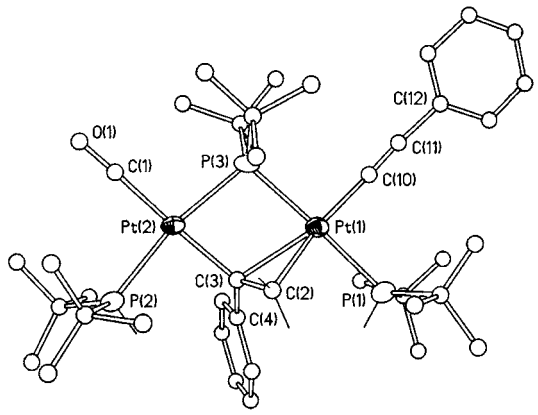

Figure 1. Molecular structure of the cation $[(\eta^1\text{-PhCC})(Bu^t_2\text{-HP})Pt(\mu\text{-}PBu^t_2)(\mu,\eta^1{:}\eta^2\text{-C(Ph)=CH}_2)Pt(CO)(PBu^t_2H)]^+$ ($(\mathbf{3})^+$). Only the Pt and P atoms are represented by 30% ellipsoids, and most of the hydrogens are omitted for clarity. Main bond distances (Å) and angles (deg): Pt(1)−C(10), 1.96(3); Pt(1)−P(1), 2.340(7); Pt(1)−P(3), 2.352(7); Pt(1)−C(2), 2.25(2); Pt(1)−C(3), 2.37(2); Pt(2)−C(3), 2.07(2); Pt(2)−P(3), 2.361(7); Pt(2)−C(1), 1.92(2); Pt(2)−P(2), 2.365(7); C(2)−C(3), 1.39(3); C(3)−C(4), 1.50(3); C(10)−Pt(1)−C(2), 162.1(10); C(10)−Pt(1)−P(1), 87.7(9); C(2)−Pt(1)−P(1), 86.8(7); C(10)−Pt(1)−P(3), 94.3(9); C(2)−Pt(1)−P(3), 91.9(7); P(1)−Pt(1)−P(3), 177.2(2); C(10)−Pt(1)−C(3), 162.4(10); C(2)−Pt(1)−C(3), 35.0(8); P(1)−Pt(1)−C(3), 102.9(6); P(3)−Pt(1)−C(3), 74.8(6); C(1)−Pt(2)−C(3), 177.3(9); C(1)−Pt(2)−P(3), 97.7(7); C(3)−Pt(2)−P(3), 80.3(7); C(1)−Pt(2)−P(2), 93.4(7); C(3)−Pt(2)−P(2), 88.4(7); P(3)−Pt(2)−P(2), 167.7(2); C(3)−C(2)−Pt(1), 77.4(13); C(2)−C(3)−C(4), 119(2); C(2)−C(3)−Pt(2), 118.5(16); C(4)−C(3)−Pt(2), 120.2(17); C(2)−C(3)−Pt(1), 67.6(13); C(4)−C(3)−Pt(1), 108.6(15); Pt(2)−C(3)−Pt(1), 106.5(10).

(2) Å), which are also terminally bonded to a secondary phosphine (pseudo-trans with respect to the bridging P nucleus) and a carbonyl (Pt(2)−C(1) = 1.92(2) Å) or a linear η^1-alkynyl (Pt(1)−C(10) = 1.96(3) Å) in a pseudo-cis fashion to P_μ. The coordination spheres are completed by a bridging $PhCCH_2$ vinyl group σ-bonded to Pt(2) and π-bonded to Pt(1) (Pt(2)−C(3) = 2.07(2) Å, Pt(2)···C(2) = 3.00(2) Å, Pt(1)−C(2) = 2.25(2) Å, Pt(1)-C(3) = 2.37(2) Å). All NMR spectra suggest that the structure is maintained in solution. Complex **3** is air- and moisture-stable and does not reductively eliminate on warming the ene−yne by coupling of the carbyl moieties. The more electrophilic center of the cation is the carbonyl ligand, as indicated by the reactions with nucleophiles. Actually, complex **3** reacts with $NaBH_4$ and CH_3OLi to give the corresponding acyl derivatives **4** and **5**, respectively. The formyl complex $(\eta^1\text{-PhCC})(Bu^t_2\text{-HP})Pt(\mu\text{-}PBu^t_2)(\mu,\eta^1{:}\eta^2\text{-C(Ph)=CH}_2)Pt(CHO)(PBu^t_2H)$ (**4**),[18] whose structure was unambiguously confirmed by the spectra of the labeled ^{13}CHO species (**4***),[19] exhibits a remarkably high thermal stability ($\tau_{1/2}$(dec) = 5 h); it is worth noting that formyl complexes of platinum were unknown until recently.[20] The methoxycarbonyl compound $(\eta^1\text{-PhCC})(Bu^t_2HP)Pt(\mu\text{-}PBu^t_2)(\mu,\eta^1{:}\eta^2\text{-C(Ph)=CH}_2)Pt(COOCH_3)(PBu^t_2H)$ (**5**)[21] is stable for weeks both in solution and in the solid state. On warming at room temperature complex **4** rapidly loses CO and is quantitatively converted into the hydride $(\eta^1\text{-PhCC})(Bu^t_2HP)\text{-}Pt(\mu\text{-}PBu^t_2)(\mu,\eta^1{:}\eta^2\text{-C(Ph)=CH}_2)Pt(H)(PBu^t_2H)$ (**6**).[22]

The present study confirms the ready accessibility of the protected diplatinum site in **1**. The cationic alkenyl−alkynyl complex **3**, obtained in the stepwise activation of 1-alkynes, and its neutral acyl and hydride derivatives **4**−**6** are interesting polyfunctional dinuclear compounds. Further studies are in progress aimed at comparing the reactivities of the various functions and promoting C−C coupling reactions.

Acknowledgment. The Consiglio Nazionale delle Ricerche (CNR) and MURST, Programmi di Interesse Nazionale (2000−2001), are gratefully acknowledged for financial support.

Supporting Information Available: Tables of crystal data, positional parameters for non-hydrogen and hydrogen atoms, bond distances and angles, and anisotropic thermal parameters and an ORTEP view with the full numbering scheme for the structure of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Complex **4** was isolated (58% yield) as a pale yellow, unstable solid by reacting **3** with a 10-fold excess of $NaBH_4$ in methanol. **4*** was prepared analogously by starting from **3***. **4**: ^{1}H NMR (C_6D_6, 293 K) δ (ppm)# 0.73, 1.18, 1.33, 1.36, 1.92, 1.93 (all d, $^3J_{HP}$ = 13.7−14.3 Hz, 54 H, PCCH_3), 3.77 (d, $^1J_{HP_2}$ = 330, $^2J_{HPt_2}$ = 22 Hz, 1 H, P_2H), 4.91 (d, $^1J_{HP_1}$ = 410, $^2J_{HPt_1}$ = 13 Hz, 1 H, P_1H), 4.12 (m, 1 H, PhCC(*H*)H), 5.74 (m, $^2J_{HPt}$ = 43 Hz, 1 H, PhCC(H)*H*), 7.09 (m, 6 H, Ph), 7.51 (d, 2 H, Ph), 7.79 (d, 2 H, Ph), 15.4 (dd, $^3J_{HP}$ = 4.3, 12.9, $^2J_{HPt_2}$ = 334 Hz, 1 H, C*H*O); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ (ppm)# −35.3 (dd, $^2J_{P_3P_1}$ = 324, $^2J_{P_3P_2}$ = 237, $^1J_{P_3Pt_1}$ = 2167, $^1J_{P_3Pt_2}$ = 2633 Hz, P_3), 46.9 (dd, $^2J_{P_2P_3}$ = 237, $^3J_{P_2P_1}$ = 7.8, $^1J_{P_2Pt_2}$ = 2168 Hz, P_2), 55.4 (dd, $^2J_{P_1P_3}$ = 324, $^3J_{P_1P_2}$ = 7.8, $^1J_{P_1Pt_1}$ = 2203 Hz, P_1), further splitting in the H-coupled spectrum for the signals at 43.9 (ddd, $^1J_{P_2H}$ = 330 Hz) and at 55.4 (ddd, $^1J_{P_1H}$ = 410 Hz); ^{195}Pt{^{1}H} NMR (C_6D_6, 293 K) δ (ppm) −3700 (dd, $^1J_{Pt_2P_3}$ = 2633, $^1J_{Pt_2P_2}$ = 2168 Hz, Pt_2), −4254 (dd, $^1J_{Pt_1P_3}$ = 2167, $^1J_{Pt_1P_1}$ = 2203 Hz, Pt_1), further splitting in the H-coupled spectrum for the signals at −3700 ppm (ddd, $^1J_{Pt_2H}$ = 334 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ (ppm)# 29.9−34.5 (m, PCCH_3), 35.5, 35.9, 36.1, 36.5, 37.0, 37.9 (w s, PCCH_3), 93.6 (w s, PhCCH_2), 102.2 (w br s, J_{CPt} = 770 Hz, PhC*C*), 124.7, 127.3, 128.4, 130.1, 130.8 (all s, Ph), 217.0 (w s, *C*=O), further splitting in the H-coupled spectrum for the signals at 217.0 ppm (d, $^1J_{CH}$ = 158 Hz); IR (KBr, Nujol) 1639 s ($\nu_{C=O}$) cm^{-1}.

(19) **4***: same signals as **4** except those at 15.4 ppm (ddd) in the ^{1}H NMR, which split further due to $^1J_{HC}$ = 158 Hz, and at 217.0 ppm in the ^{13}C{^{1}H} (strong s, $^1J_{CPt_2}$ = 1021 Hz) and ^{13}C (strong d, $^1J_{HC}$ = 158, $^1J_{CPt_2}$ = 1021 Hz) NMR spectra. The $\nu_{C=O}$ absorption is shifted to 1607 cm^{-1} in the IR spectrum.

(20) Leoni, P.; Marchetti, F.; Marchetti, L.; Pasquali, M.; Quaglierini, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3617.

(21) Complex **5** was isolated (64% yield) as a colorless, stable solid by reacting **3** with a 5-fold excess of $LiOCH_3$ in methanol. Anal. Calcd for $C_{42}H_{71}O_2P_3Pt_2$: C, 46.2; H, 6.56. Found: C, 45.8; H, 6.72. **5**: ^{1}H NMR (C_6D_6, 293 K) δ (ppm) 0.86, 1.28, 1.30, 1.38, 2.01, 2.06 (all d, $^3J_{HP}$ = 14.3−16.0 Hz, 54 H, PCCH_3), 3.47 (s, 3 H, OCH_3), 3,71 (d, $^1J_{HP_2}$ = 340 Hz, 1 H, P*H*), 4.63 (d, $^1J_{HP_1}$ = 392 Hz, 1 H, P*H*), 4.92 (m, 1 H, PhCC(H)*H*), 5.65 (m, 1 H, PhCC(*H*)H), 7.11 (m, 6 H, Ph), 7.69 (d, 2 H, Ph), 7.81 (d, 2 H, Ph); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ (ppm)# −45.3 (dd, $^2J_{P_3P_1}$ = 318, $^2J_{P_3P_2}$ = 262, $^1J_{P_3Pt_2}$ = 2318, $^1J_{P_3Pt_1}$ = 1750 Hz, P_3), 47.1 (d, $^2J_{P_2P_3}$ = 262, $^1J_{P_2Pt_2}$ = 1861 Hz, P_2), 55.5 (d, $^2J_{P_1P_3}$ = 318, $^1J_{P_1Pt_1}$ = 2168 Hz, P_1); IR (KBr, Nujol) 1652 s ($\nu_{C=O}$) cm^{-1}.

(22) Complex **6** was isolated (70% yield) as a yellow, stable solid after stirring for 3 days at room temperature a toluene solution of **4**. Anal. Calcd for $C_{40}H_{69}P_3Pt_2$: C, 46.5; H, 6.73. Found: C, 46.8; H, 6.68. **6**: ^{1}H NMR (CD_2Cl_2, 293 K) δ (ppm)# −9.75 (dd, $^2J_{HP}$ = 4.4, 18.0, $^1J_{HPt_2}$ = 1415 Hz, 1 H, Pt*H*), 0.81, 1.27, 1.31, 1.41, 1.56, 1.62 (all d, J_{HP} = 13.3−14.1 Hz, 54 H, PCCH_3), 2.75 (d, $^1J_{HP_3}$ = 332 Hz, 1 H, P*H*), 4.10 (dd, $^1J_{HP_2}$ = 314, $^3J_{HP_3}$ = 4.2, $^2J_{HPt_2}$ = 19 Hz, 1 H, P*H*), 4.17 (m, J_{HPt} = 47 Hz, 1 H, PhCC(*H*)H), 4.90 (d, J_{HP} = 3, J_{HPt} = 24, 38 Hz, 1 H, PhCC(H)*H*), 7.0−7.2, 7.4, 7.7 (m, 10 H, Ph).; ^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ (ppm)# −34.2 (dd, $^2J_{P_3P_1}$ = 318, $^2J_{P_3P_2}$ = 278, $^1J_{P_3Pt_1}$ = 2160, $^1J_{P_3Pt_2}$ = 2293 Hz, P_3), 64.6 (dd, $^2J_{P_2P_3}$ = 278, $^3J_{P_2P_1}$ = 8.2, $^1J_{P_2Pt_2}$ = 2020 Hz, P_2), 58.2 (dd, $^2J_{P_1P_3}$ = 318, $^3J_{P_1P_2}$ = 8.2, $^1J_{P_1Pt_1}$ = 2139 Hz), further splitting in the H-coupled spectrum for the signals at 64.6 (ddd, $^1J_{P_2H}$ = 300 Hz) and 58.2 (ddd, $^1J_{P_2H}$ = 314 Hz); ^{195}Pt{^{1}H} NMR (C_6D_6, 293 K) δ (ppm) −4628 (dd, $^1J_{Pt_2P_3}$ = 2293, $^1J_{Pt_2P_2}$ = 2020 Hz, Pt_2), −4249 (dd $^1J_{Pt_1P_3}$ = 2160, $^1J_{Pt_1P_1}$ = 2139 Hz, Pt_1), further splitting in the H-coupled spectrum for the signals at -4628 (ddd, $^1J_{Pt_2H}$ = 1412 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K) δ (ppm) 30.0, 31.1, 32.7, 33.6 (all br s, PCCH_3) 34.0−37.0 (w br m, PCCH_3), 93.6 (w s, J_{CPt} = 65 Hz, PhCCH_2), 117.3 (s, J_{CPt} = 267 Hz, PhC*C*), 124.1, 126.5, 126.9, 128.0, 129.5, 130.3 (all s, Ph), 151.3 (w br s, J_{CPt} = 20 Hz, PhCCH_2); IR (KBr, Nujol) 2120 w (ν_{CC}), 2096 s (ν_{PtH}) cm^{-1}.