New Acetonyl Palladium(II) Complexes

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$[Pd\{CH_2C(O)Me\}Cl]_n$ (**1**), reacts with P- and N-donor ligands to afford *cis*-$[Pd\{CH_2C(O)Me\}Cl(dppf)]$ (dppf = bis(diphenylphosphino)ferrocene (**2**)) and $[Pd\{CH_2C(O)Me\}ClL_2]$ (L = pyridine = py (**3**), 4-Me-pyridine = Mepy (**4**), 4-^{t}Bu-pyridine = ^{t}Bupy (**5**)). Reaction of **3** or **3**−**5** with 1 equiv of [Tl(acac)] or TlTfO and L affords, respectively, $[Pd\{CH_2C(O)Me\}(O,O\text{-acac})(py)]$ (**6**) or $[Pd\{CH_2C(O)Me\}L_3]TfO$ (L = py (**7**), Mepy (**8**), ^{t}Bupy (**9**)). The reaction of **9** with 1 equiv of $\{Ph_2P(CH_2)_2\}_2PhP$ (triphos) gave $[Pd\{CH_2C(O)Me\}(triphos)]TfO$ (**10**). Complex **1** reacts with norbornene (nbn) followed by addition of L_2 (1:2:1), with 1,5-cyclooctadiene (cod) (1:1) or with 1,1-dimethyl allene (dma) to give $[Pd\{(nbn)CH_2C(O)Me\}ClL_2]$ (L_2 = 2,2′-bipyridine (bpy) (**11**), 4,4′-di-*tert*-butyl 2,2′-bipyridine (dbbpy) (**12**)), $[Pd\{CH_2C(O)Me\}Cl(cod)]$ (**13**), or $[Pd\{\eta^3\text{-}CH_2C\{CH_2C(O)Me\}Cl]_2$ (**14**), respectively. The structures of complexes **3**, **8**, **11**, and **13** have been solved by X-ray diffraction studies.

Introduction

We are involved in the synthesis of ketonyl metal complexes[1–7] because some of these species are intermediates in organic synthesis.[8–10]

We have reported the synthesis of the polymer $[Pd\{CH_2C(O)Me\}Cl]_n$ (**1**), obtained by transmetalation reactions from $[Hg\{CH_2C(O)Me\}_2]$ and $[PdCl_2(MeCN)_2]$ or $(NMe_4)[Pd_2Cl_6]$.[4] The other methods of synthesis of acetonyl palladium(II) complexes lead to neutral species always containing strongly coordinated ligands, such as PPh_3,[11] *N,N,N′,N′*-tetramethylethylenediamine,[3] C_6F_5, $C_6H_4CH_2NMe_2$-2.[12] In contrast with these complexes, **1** offers the opportunity of preparing neutral acetonyl complexes simply by bridging splitting reactions with neutral ligands or cationic acetonyl complexes by replacing the chloro ligand, which leaves available for substitution three coordination positions at palladium. We have used **1** to prepare neutral mono- and dinuclear complexes as well as C-palladated β-ketoenamine complexes resulting from insertion of one molecule of isocyanide into the Pd−acetonyl bond.[4,5]

We describe our last report on the synthetic use of **1**, showing the preparation of new types of neutral and the first cationic acetonyl complexes resulting from its reaction with a variety of ligands (neutral and anionic, monodentate N donor, di- and tridentate P donor). The insertion of alkenes into Pd−C bonds has attracted interest, since it constitutes a key step in many important processes such as the Heck reaction,[9,13] the palladium-catalyzed polimerization of olefins,[14,15] and the copolymerization

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of alkenes and CO.[15,16] However, only a few examples of alkene insertion into the Pd−ketonyl bond have been reported.[10,17] We describe here a complex resulting from insertion of an alkene (norbornene) into the Pd−acetonyl bond and its crystal structure, which is the first example of a fully characterized palladium complex of this type.

Allenes have found increasing applications in transition metal-catalyzed reactions for organic and polymer synthesis.[18] Organopalladium complexes react with allenes to afford π-allyl complexes.[19–21] We also report the first example of a reaction affording a π-allyl complex resulting after insertion of an allene into a Pd−ketonyl bond.

Experimental Section

Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Molar conductivities were measured on a ca. 5×10^{-4} M acetone solution with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded in a Brucker AC 200 or Avance 300 or 400 spectrometers at room temperature. Chemical shifts were referred to TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F). When needed, NMR assignments were performed with the help of APT, DEPT, COSY, one-dimensional NOE experiments, and HETCOR techniques. Complex **1** was prepared as reported previously.[4]

Synthesis of [Pd{CH$_2$C(O)Me}Cl(dppf)] (2). To a suspension of **1** (100 mg, 0.50 mmol) in dry THF (2 mL) was added bis(diphenylphosphino)ferrocene (dppf) (279 mg, 0.50 mmol) under N_2. The mixture was stirred for 15 min, the solution was concentrated to dryness, and Et_2O (20 mL) was added. The resulting suspension was filtered and the solid washed with Et_2O (10 mL) to give **2** as an orange solid. Yield: 337 mg, 90%. Mp: 140 °C. IR (Nujol, cm^{-1}): ν(C=O) 1640; ν(Pd−Cl) 294. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.97−7.88 (m, 4H, Ph), 7.69−7.59 (m, 4H, Ph), 7.46−7.37 (m, 8H, Ph), 7.29−7.20 (m, 4H, Ph), 4.73 (m, 2H, Cp), 4.52 (m, 2H, Cp), 4.13 (m, 2H, Cp), 3.33 (m, 2H, Cp), 2.70 (dd, 2H, CH$_2$, $^2J_{HPcis}$ = 5.2 Hz, $^2J_{HPtrans}$ = 12.6 Hz), 2.27 (s, 3H, Me). ^{31}P{^{1}H} NMR (80.95 MHz, CDCl$_3$): δ 38.42 (J_{PP} = 29 Hz), 17.2 (d, $^2J_{PP}$ = 29 Hz). Anal. Calcd for $C_{37}H_{33}ClFeNOP_2Pd$: C, 58.99; H, 4.42. Found: C, 58.63; H, 4.53.

Synthesis of [Pd{CH$_2$C(O)Me}Cl(py)$_2$] (3). To a suspension of **1** (195 mg, 0.98 mmol) in acetone (40 mL) was added pyridine (171 μL, 2.11 mmol). The suspension was stirred until **1** dissolved and then was filtered through Celite. The filtrate was concentrated (ca. 2 mL), and addition of Et_2O (20 mL) gave a suspension that was filtered off. The solid was washed with Et_2O (2 × 5 mL) and air-dried to give **3** as a yellow solid. Yield: 322 mg, 92%. Mp: 114−116 °C. IR (Nujol, cm^{-1}): ν(C=O) 1636 (s); ν(Pd−Cl) 280 (m). ^{1}H NMR (200 MHz, CDCl$_3$, trans:cis isomers 10:1): trans isomer δ 8.86 (m, 4H, *o*-H), 7.80 (m, 2H, *p*-H), 7.40 (m, 4H, *m*-H), 2.64 (s, 2H, CH$_2$), 1.72 (s, 3H, Me); cis isomer δ 8.73 (m, 2 H, *o*-H, py cis to acetonyl), 8.41 (m, 2 H, *o*-H, py trans to acetonyl), 7.80 (m, 1 H, *p*-H, py trans to acetonyl), 7.70 (m, 2 H, *p*-H, py cis to acetonyl), 7.40 (m, 2 H, *m*-H, py cis to acetonyl), 7.25 (m, 2 H, *m*-H, py trans to acetonyl), 2.81 (s, 2H, CH$_2$), 2.37 (s, 3H, Me). ^{13}C{^{1}H} NMR (50.32 MHz, CDCl$_3$): trans isomer δ 209.3 (CO), 152.7 (*o*-C), 138.0 *p*-C), 125.2 (*m*-C), 32.1 (CH$_2$), 30.0 (Me); cis isomer δ 153.2 (py), 152.2 (py), 138.5 (py), 125.7 (py), 124.8 (py), 30.8 (Me), 22.9 (CH$_2$). Anal. Calcd for $C_{13}H_{15}ClN_2OPd$: C, 43.72; H, 4.23; N, 7.84. Found: C, 43.45; H, 4.21; N, 7.82. Single crystals of **3** were obtained by slow diffusion of Et_2O into a solution of **3** in CHCl$_3$.

Synthesis of [Pd{CH$_2$C(O)Me}Cl(Mepy)$_2$] (4). This yellow complex was prepared as described for **3**, using **1** (100 mg, 0.50 mmol) in CH$_2$Cl$_2$ (10 mL) and 4-methyl pyridine (Mepy, 104 μL, 1.06 mmol). Yield: 174 mg, 90%. Dec pt: 126−128 °C. IR (Nujol, cm^{-1}): ν(C=O) 1638 (s); ν(Pd−Cl) 270 (m). ^{1}H NMR (300 MHz, CDCl$_3$, trans:cis isomers 10:1): trans isomer δ 8.64−8.66 (m, 4H, *o*-H), 7.18−7.2 (m, 4H, *m*-H), 2.61 (s, 2H, CH$_2$), 2.40 (s, 6H, *Me*py), 1.74 (s, 3H, *Me*CO); cis isomer δ 8.52 (m, 2H, *o*-H), 8.26 (m, 2H, *o*-H), 2.75 (s, 2H, CH$_2$). ^{13}C{^{1}H} NMR (75.43 MHz, CDCl$_3$): trans isomer δ 209.3 (CO), 152.0 (CH), 150.0 (C), 126.1 (CH), 32.0 (CH$_2$), 30.1 (*Me*CO), 21.0 (*Me*py); cis isomer δ 152.4 (*o*-C), 151.4 (*o*-C), 126.5 (*m*-C), 30.8 (*Me*CO), 23.0 (CH$_2$), 21.0 (*Me*py). Anal. Calcd for $C_{15}H_{19}ClN_2OPd$: C, 46.77; H, 4.97; N, 7.27. Found: C, 46.40; H, 4.88; N, 7.14.

Synthesis of [Pd{CH$_2$C(O)Me}Cl(^{t}Bupy)$_2$] (5). This complex was prepared as described for **3**, using **1** (150 mg, 0.75 mmol) in CH$_2$Cl$_2$ (10 mL) and 4-*tert*-butylpyridine (^{t}Bupy, 234 μL, 1.58 mmol). The final solution was concentrated (ca. 2 mL) and cooled in a water/ice bath. Addition of *n*-pentane (15 mL) and vigorous stirring gave a suspension that was filtered off, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to give **5** as a light-yellow solid. Yield: 324 mg, 91.5%. Dec pt: 128 °C. IR (Nujol, cm^{-1}): ν(C=O) 1638 (s); ν(Pd−Cl) 278 (m). ^{1}H NMR (300 MHz, CDCl$_3$ trans:cis isomers 12:1): trans isomer δ 8.72−8.70 (m, 4H), 7.34−7.36 (m, 4H), 2.64 (s, 2H, CH$_2$), 1.73 (s, 3H, *Me*CO), 1.31 (s, 18H, ^{t}Bu); cis isomer δ 8.59 (m, 2H, *o*-H), 8.29 (m, 2H, *o*-H), 7.23 (m, 2H), 2.78 (s, 2H, CH$_2$), 2.37 (s, 3H, *Me*CO). ^{13}C{^{1}H} NMR (75.43 MHz, CDCl$_3$): trans isomer δ 209.3 (CO), 162.3 (C*p*), 151.8 (*o*-C), 122.2 (*m*-C), 35.0 (*C*Me$_3$), 31.8 (CH$_2$), 30.0 (C*Me$_3$*), 30.0 (*Me*CO); cis isomer δ 152.5 (*o*-C), 151.5 (*o*-C), 122.8 (*m*-C), 121.8 (*m*-C), 30.9 (*Me*CO), 22.9 (CH$_2$). Anal. Calcd for $C_{21}H_{31}ClN_2OPd$: C, 53.74; H, 6.66; N, 5.97. Found: C, 53.35; H, 6.69; N, 5.86.

Synthesis of [Pd{CH$_2$C(O)Me}(acac)(py)] (6). To a solution of **3** (90 mg, 0.25 mmol) in acetone (25 mL) was added Tl(acac) (77 mg, 0.25 mmol). The resulting suspension was stirred for 15 min and filtered through Celite. The filtrate was concentrated to dryness, and *n*-hexane (5 mL) was slowly added to give an oil that was stirred in an acetone/ice bath to give a solid, which was filtered off, washed with *n*-hexane (5 mL), and air-dried to give **6** as a yellow solid. Yield: 40 mg, 46%. Mp: 67−68 °C. IR (cm^{-1}): ν(C=O) 1650; ν(C=O, acac) 1582, 1516. ^{1}H RMN (200 MHz, CDCl$_3$): δ 8.79−8.83 (m, 2H, py), 7.73−7.82 (m, 1H, py),

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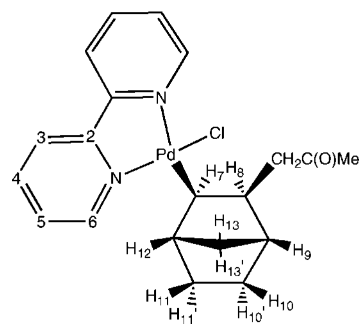
7.33−7.40 (m, 2H, py), 5.35 (s, 1H, acac), 2.64 (s, 2H, CH_2), 2.20 (s, 3H, *Me*$COCH_2$), 2.00 (s, 3H, Me, acac), 1.93 (s, 3H, Me, acac). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 212.6 (Me*C*OCH_2), 187.6 and 185.4 (CO, acac), 152.4 (*o*-C), 137.5 (C*p*), 125.0 (*m*-C), 99.9 (*C*H, acac), 30.2 (*Me*$COCH_2$), 27.7 (Me, acac), 27.1 (Me, acac), 26.5 (CH_2). Anal. Calcd for $C_{13}H_{17}NO_3Pd$: C, 45.70; H, 5.01; N, 4.10. Found: C, 45.40; H, 5.02; N, 4.07.

Synthesis of [Pd{$CH_2C(O)Me$}$(py)_3$]TfO (7). TlOTf (103 mg, 0.29 mmol) was added to a solution of **3** (100 mg, 0.28 mmol) in acetone (20 mL). Pyridine (25 μL, 0.3 mmol) was added to the resulting suspension, which was stirred for 15 min and concentrated to dryness, and CH_2Cl_2 was added (20 mL). The resulting suspension was stirred for 20 min and filtered through Celite. The filtrate was concentrated (ca. 3 mL) and Et_2O was slowly added. The mixture, containing an oil, was stirred for 1 h at 0 °C to give a suspension, which was filtered off. The solid was washed with Et_2O (2 × 5 mL), recrystalized from CH_2Cl_2/Et_2O, and air-dried to give **7** as a yellow solid. Yield: 125 mg, 81%. Mp: 102−104 °C. Λ_M (acetone, 4.7 × 10^{-4} M): 149 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(C═O) 1650 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 8.98−8.97 (m, 4H, py cis to acetonyl), 8.67−8.65 (m, 2H, py trans to acetonyl), 7.86−7.81 (m, 2H, py cis to acetonyl), 7.74−7.69 (m, 1H, py trans to acetonyl), 7.48−7.43 (m, 4H, py cis to acetonyl), 7.36−7.32 (m, 2H, py trans to acetonyl), 2.60 (s, 2H, CH_2), 1.78 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 211.6 (CO), 152.3 (C py cis to acetonyl), 149.8 (C py trans to acetonyl), 138.7 (C py cis to acetonyl), 138.5 (C py trans to acetonyl), 126.2 (C py cis to acetonyl), 125.9 (C py trans to acetonyl), 30.6 (Me), 28.1(CH_2). Anal. Calcd for $C_{19}H_{20}ClF_3N_3O_4PdS$: C, 41.50; H, 3.67; N, 7.64; S, 5.83. Found: C, 41.30; H, 3.40; N, 7.60; S, 5.63.

Synthesis of [Pd{$CH_2C(O)Me$}$(Mepy)_3$]TfO·H_2O (8). To a suspension of **1** (150 mg, 0.75 mmol) in acetone (7 mL) were added Mepy (240 μL, 2.46 mmol) and TlTfO (271 mg, 0.77 mmol). The resulting suspension was stirred for 30 min and then was filtered through Celite. The filtrate was concentrated to dryness, extracted with CH_2Cl_2 (20 mL), and filtered through Celite. The filtrate was concentrated (ca. 1 mL) and Et_2O (5 mL) was added. The mixture, containing an oil, was stirred in an acetone/ice bath to give a suspension, which was filtered off to give **8** as a colorless solid. Yield: 373 mg, 81%. Mp: 94 °C. Λ_M (acetone, 4.72 × 10^{-4}): 120 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═O) 1650; ν(OH) 3426. ^1H NMR (300 MHz, $CDCl_3$): δ 8.74−8.72 (m, 4H, py cis to R), 8.39−8.37 (m, 2H, py trans to R), 7.27−7.24 (m, 4H, py cis to R), 7.14−7.12 (m, 2H, py trans to R), 2.54 (s, 2H, CH_2), 2.39 (s, 6H, *Me*py cis to R), 2.27 (s, 3H, *Me*py trans to R), 1.76 (s, 3H, *Me*CO). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 212.2 (CO), 151.5 (CH py cis to R), 151.13 (C py cis to R), 150.70 (C py trans to R), 149.2 (CH py trans to R), 127.1 (CH py cis to R), 126.8 (CH py trans to R), 30.7 (*Me*CO), 27.8 (CH_2), 21.1 (*Me*py cis to R), 21.0 (*Me*py trans to R). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ −78.14. Anal. Calcd for $C_{22}H_{28}F_3N_3O_5PdS$: C, 43.32; H, 4.63; N, 6.89; S, 5.26. Found: C, 43.34; H, 4.55; N, 6.99; S, 5.02. Single crystals of **8**·H_2O were obtained by slow diffusion of Et_2O into a solution of **8** in acetone.

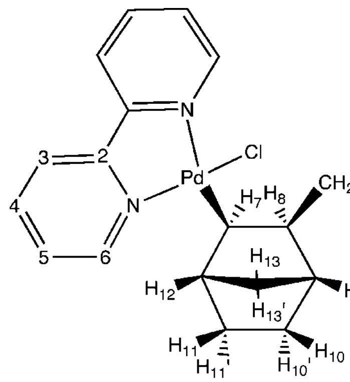
Synthesis of [Pd{$CH_2C(O)Me$}(^{t}Bupy)$_3$]TfO (9). To a suspension of **1** (88 mg, 0.44 mmol) in acetone (3 mL) was added ^{t}Bupy (0.2 mL, 1.35 mmol). Addition of KTfO (88 mg, 0.46 mmol) gave a suspension, which was concentrated to dryness, extracted with CH_2Cl_2 (5 mL), and filtered through Celite. The filtrate was concentrated to dryness and *n*-pentane (10 mL) was added. The mixture, containing an oil, was stirred in an acetone/ice bath to give a suspension, which was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **9** as a colorless solid. Yield: 240 mg, 76%. Mp: 119 °C. Λ_M (acetone, 4.8 × 10^{-4}): 109 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═O) 1644. ^1H NMR (300 MHz, $CDCl_3$): δ 8.83−8.81 (m, 4H, py cis to R), 8.47−8.50 (m, 2H, py trans to R), 7.43−7.41 (m, 4H, py cis to R), 7.31−7.28 (m, 2H, py trans to R), 2.53 (s, 2H, CH_2), 1.72 (s, 3 H, Me), 1.29 (s, 18 H, ^{t}Bu), 1.21 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (50.30 MHz, $CDCl_3$): δ 212.6 (CO), 163.5 (C py cis to R), 162.9 (C py trans to R), 151.70 (CH py cis to R), 149.4 (CH py trans to R), 123.3 (CH py cis to R), 122.9 (CH py trans to R), 35.1 (*C*Me_3, cis to R), 35.0 (*C*Me_3, trans to R), 30.6 (*Me*CO), 30.1 (C*Me_3*), 27.8 (CH_2). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ −78.14. Anal. Calcd for $C_{31}H_{44}F_3N_3O_4PdS$: C, 51.84; H, 6.18; N, 5.85; S, 4.46. Found: C, 51.42; H, 6.19; N, 6.10; S, 4.07.

Synthesis of [Pd{$CH_2C(O)Me$}(triphos)]TfO·0.5THF (10). To a solution **9** (81.7 mg, 0.11 mmol) in dry THF (4 mL) was added $\{Ph_2P(CH_2)_2\}_2PhP$ (triphos, 61 mg, 0.11 mmol) under N_2. After 15 min the solution was concentrated and Et_2O (2 mL) was added. The resulting suspension was filtered off, and the solid was washed with Et_2O (5 mL) and air-dried to give **10** as a colorless solid. Yield: 77 mg, 74%. Mp: 182−184 °C. Λ_M (acetone, 5 × 10^{-4}): 158 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═O) 1628. ^1H NMR (300 MHz, $CDCl_3$): δ 7.71−7.38 (m, 25H, Ph), 3.74 (m, 2H, CH_2, THF), 3.38−3.33 (m, 2H, CH_2, triphos), 3.23−3.18 (m, 2H, CH_2, triphos), 3.10−2.78 (m, 2H, CH_2, triphos), 2.50−2.38 (m, 2H, CH_2, triphos), 2.51 (dt, 2H, *CH_2*C(O), $^3J_{HPcis}$ = 5.1 Hz, $^3J_{HPtrans}$ = 10.2 Hz), 1.85 (m, 2H, CH_2, THF). 1.21 (s, 3H, Me). $^{31}P\{^1H\}$ (121.42 MHz, $CDCl_3$): δ 110.1 (t, P trans to R, $^2J_{PP}$ = 19.6 Hz), 48.3 (d, P cis to R, $^2J_{PP}$ = 19.6 Hz). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 210.3 (CO), 133.4−131.9 (m, CH, Ph) 129.7−129.3 (m, CH, Ph), 128.6−127.4 (m, C, Ph), 67.9 (THF), 35.0 (dt, *C*H_2CO, $^2J_{CPtrans}$ = 62 Hz, $^2J_{CPcis}$ = 3.3 Hz), 30.0 (Me), 26.0 (dt, CH_2, triphos, $^2J_{CP}$ = 62 Hz, $^2J_{CPcis}$ = 3.3 Hz), 25.5 (THF). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ −78.1. Anal. Calcd for $C_{40}H_{42}F_3O_{4.5}PdP_3S$: C, 54.40; H, 4.79; S, 3.63. Found: C, 54.01; H, 4.73; S, 3.49.



Synthesis of [Pd{$C_7H_{10}[CH_2C(O)Me]$}Cl(bpy)] (11). To a solution of norbornene (110 mg, 1.16 mmol) in dry MeCN (3 mL) was added **1** (116 mg, 0.58 mmol) under N_2. The resulting suspension was stirred for 1 h and filtered under N_2. Bpy (91 mg, 0.58 mmol) was added to the filtrate to give a suspension, which was filtered off. The filtrate was concentrated (0.5 mL), Et_2O (10 mL) was added, and the precipitate was filtered off; the solid was washed with Et_2O (3 mL) and air-dried to give **11** as a yellow solid. Yield: 131 mg, 50%. Dec pt: 149 °C. IR (cm^{-1}): ν(C═O) 1704; ν(Pd−Cl) 318.^1H NMR (400 MHz, $CDCl_3$): δ 9.35 (m, 1H, H6′), 8.80 (m, 1H, H6), 8.40−8.02 (m, 3H, bpy, H3, H3′, H4), 7.95 (m, 1H, H4′), 7.63 (m, 1H, H5), 7.51 (m, 1H, H5′), 3.47 (dd, 1H, $CH_2C(O)$, $^2J_{HH}$ = 17.3, $^3J_{HH}$ = 6.2 Hz), 2.83 (dd, 1H, $CH_2C(O)$, $^2J_{HH}$ = 17.3, $^3J_{HH}$ = 7.9 Hz), 2.52 (m, 1H, H12), 2.46 (m, 1H, H7), 2.22 (m, 2H, H8 and H13), 2.07 (s, 3H, Me), 1.87 (m, 1H, H9), 1.59 (m, 1H, H10′), 1.31 (m, 2H, H10 and H11), 1.16 (m, 1H, H13′), 1.11 (m, 1H, H11′). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 210.1 (CO), 155.9 (C, bpy), 152.4 (C, bpy), 149.2 (C6′), 148.9 (C6), 138.4 (C4), 138.3 (C4′), 126.4 (C5), 126.1 (C5′), 122.1 (C3 or C3′), 121.1 (C3 or C3′), 51.5 (C7), 50.9 (*C*H_2CO), 46.3 (C12), 46.1 (C8), 42.7 (C9), 36.3 (C13), 31.5 (Me), 31.2 (C11), 29.5 (C10). Anal. Calcd for $C_{20}H_{23}ClN_2OPd$: C, 53.47; H, 5.16; N, 6.24. Found: C, 53.14; H, 5.15; N, 6.42. Single crystals of **11** were obtained by slow diffusion of Et_2O into a solution of **11** in acetone.

Synthesis of [Pd{$C_7H_{10}[CH_3C(O)Me]$}Cl(dbbpy)] (12). To a solution of **1** (127 mg, 0.635 mmol) in dry MeCN (5 mL) was

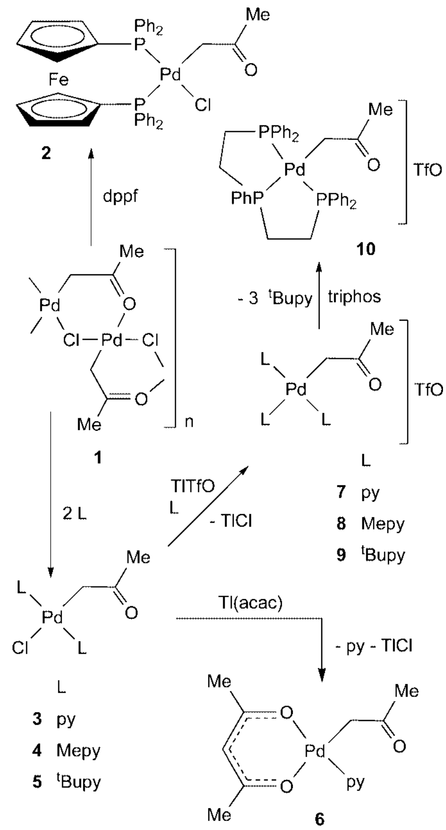


added norbornene (120 mg, 1.27 mmol) under N_2. The resulting suspension was stirred for 1 h and then filtered through Celite. To the filtrate was added dbbpy (170 mg, 0.635 mmol) to give a suspension, which was concentrated (3 mL) and then filtered off, washed with *n*-pentane (5 mL), and air-dried, to give **12** as a yellow solid. The filtrate was concentrated, Et_2O was added, and the suspension was filtered to give a second crop of **12**. Yield: 170 mg, 47%. IR (cm^{-1}): ν(C=O) 1714; ν(Pd−Cl) 326. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (m, 1H, dbbpy), 8.69 (m, 1H, dbbpy), 7.96 (m, 1H, dbbpy), 7.90 (m, dbbpy), 7.59 (m, 1H, dbbpy), 7.48 (m, 1H, dbbpy), 3.45 (dd, 1H, CH_2C(O), $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 6.3 Hz), 2.89 (dd, 1H, CH_2C(O), $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 8.4 Hz), 2.50−2.47 (m, 2H, H7 and H12), 2.24−2.18 (m, 2H, H8 and H13), 2.10 (s, 3H, Me), 1.87 (m, 1H, H9), 1.60−1.53 (m, 1H, H10′), 1.44 (s, 9H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 1.35−1.25 (m, 2H, H10 and H11), 1.15 (m, 1H, H13′), 1.11 (m, 1H, H11′). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 210.4 (CO), 162.8 (C, dbbpy), 156.3 (C, dbbpy), 152.8 (C, dbbpy), 149.1 (C, dbbpy), 148.7 (C, dbbpy), 123.7 (C, dbbpy), 123.4 (C, dbbpy), 118.6 (C, dbbpy), 117.4 (C, dbbpy), 51.1 (CH_2), 50.5 (C7), 46.3 (C12), 46.2 (C8), 42.7 (C9), 36.2 (C13), 35.4 (*C*Me$_3$), 35.3 (*C*Me$_3$), 31.6 (Me), 31.3 (C11), 30.4 (C*Me*$_3$), 30.2 (C*Me*$_3$), 29.7 (C10). Anal. Calcd for $C_{28}H_{39}ClN_2OPd$: C, 59.89; H, 7.00; N, 4.99. Found: C, 58.66; H, 7.61; N, 5.01. See discussion.

Synthesis of [Pd{CH$_2$C(O)Me}Cl(cod)] (13). To a suspension of **1** (150 mg, 0.75 mmol) in dry THF (15 mL) was added cod (104 μL, 0.85 mmol) under N_2. When the solid was disolved, the reaction mixture was filtered under N_2 and the filtrate was concentrated (ca. 3 mL). Addition of *n*-pentane (20 mL) gave a suspension that was stirred in an acetone/ice bath for 20 min and filtered under N_2. The solid was washed with *n*-hexane (2 × 5 mL) and air-dried to give **13** as a yellow solid. Yield: 188 mg, 81%. Dec pt: 100 °C. IR (cm^{-1}): ν(C=O) 1648. ^{1}H NMR (200 MHz, C_6D_6): δ 5.71 (2H, CH, cod), 5.10 (2H, CH, cod), 3.00 (2H, C*H$_2$*CO), 2.53 (3H, Me), 1.40−1.81 (8H, CH_2, cod). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6): δ 208.9 (CO), 123.3 (CH, cod), 107.0 (CH, cod), 35.8 (*C*H$_2$CO), 31.3 (*Me*CO), 30.8 (*C*H$_2$, cod), 27.4 (*C*H$_2$, cod). Anal. Calcd for $C_{11}H_{17}ClOPd$: C, 43.02; H, 5.58. Found: C, 43.0; H, 5.52. Single crystals of **13** were obtained by slow diffusion of Et_2O into a solution of **13** in $CDCl_3$.

Synthesis of [Pd$_2${η^3-CH$_2$C[CH$_2$C(O)Me]CMe$_2$}$_2$(μ-Cl)$_2$] (14). A solution of **1** (106 mg, 0.54 mmol) in dry MeCN (5 mL) was stirred with 3-methyl-1,2-butadiene (63.8 μL, 0.64 mmol) under N_2 for 1 h and then filtered through Celite and concentrated to dryness. The residue was stirred with *n*-pentane (10 mL) and the resulting suspension was filtered. The solid was washed with *n*-pentane (5 mL) and air-dried to give **14** as a pale yellow solid. Yield: 110 mg, 77%. Dec pt: 180 °C. IR (cm^{-1}): ν(C=O) 1714; ν(Pd−Cl) 260, 240. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.78 (H$_A$, AB system, 1H, C*H$_2$*C(O), $^2J_{HH}$ = 17.4 Hz), 3.61 (d, 1H, CH_2, allene, $^2J_{HAHB}$ = 1.4 Hz), 3.26 (H$_B$, AB system, 1H, C*H$_2$*CO, $^2J_{HAHB}$ = 17.4 Hz), 3.25 (d, 1H, CH_2, allene, $^2J_{HH}$ = 1.4 Hz), 2.21 (s, 3H, *Me*CO), 1.32 (s, 3H, Me, allene), 1.31 (s, 3H, Me, allene). ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ 203.9 (CO), 114.9 (C), 91.4 (C), 58.7 *C*H$_2$C(O)), 48.6 (CH_2, allene), 29.9 (*Me*CO), 24.3 (Me, allene), 23.4 (Me, allene). Anal. Calcd for $C_{16}H_{26}Cl_2O_2Pd_2$: C, 35.95; H, 4.91. Found: C, 35.63; H, 4.90.

Scheme 1



X-ray Structure Determinations of Complexes 3, 8, 11, and 13. Complexes **3** and **13** were measured on a Siemmens P4 diffractometer. Structure **11** was measured on a Bruker Smart APEX diffractometer. Data were collected using monochromated Mo Kα radiation in ω scan mode. Structure **8** was measured on a Bruker Smart 1000 diffractometer in w and f scan modes. Absorption corrections were applied on the basis of psi-scans for structures **3** and **13** and multiscans (Program SADABS) for structures **8** and **11**. All structures were refined anisotropically on F^2. The methyl groups were refined using rigid groups (AFIX 137), water hydrogens in compound **8** were refined as free with DFIX, and the other hydrogens were refined using a riding model. *Special features*: Complex **8**: The triflate anion is disordered over three positions (0.67:0.24:0.09). An unexpected difference peak was tentatively identified as a water molecule. Reasonable hydrogen sites for the water could be located and refined.

Results and Discussion

Reactions of [Pd{CH$_2$C(O)Me}Cl]$_n$ (1) with P- and N-Donor Ligands to Give Neutral Complexes. The reaction of **1** with 1 equiv of bis(diphenylphosphino)ferrocene (dppf) in THF under N_2 gave *cis*-[Pd{CH$_2$C(O)Me}Cl(dppf)] (**2**) (Scheme 1) instead of the desired enolato complex that could be formed due to the strong *transphobia* between C- and P-donor ligands. Thus, the reaction of *cis*-[PdBr(Ar)(dpb)] (dpb = 1,2-bis(diphenylphosphino)benzene) with K{OC(=CMe$_2$)Ph} gives the enolato complex *cis*-[Pd(Ar){OC(=CMe$_2$)Ph}(dpb)], although most potassium enolates afford the corresponding 2-oxoalkyl derivatives.[22]

(22) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398.

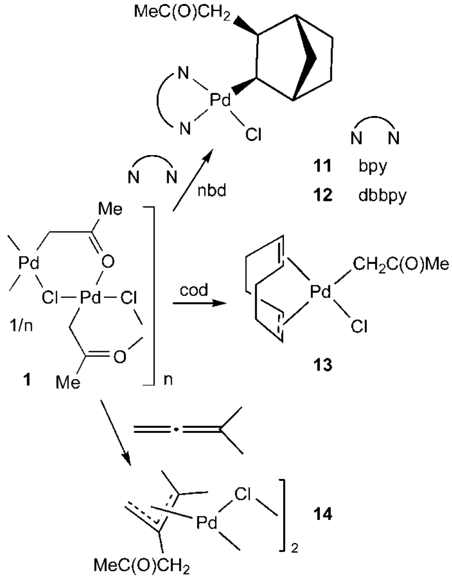
Addition of pyridine ligands (2.1:1) to suspensions of **1** in acetone affords complexes [Pd{$CH_2C(O)Me$}ClL_2] (L = py (**3**), Mepy (**4**), ^tBupy (**5**)) with good yields (>90%). Complexes **3** and **4** can be easily precipitated from their solutions by addition of Et_2O, but isolation of **5** required the use *n*-pentane as precipitating agent. We have unsuccessfully attempted to prepare dinuclear complexes containing bridging acetonyl ligands such as [Pd_2{$CH_2C(O)Me$}{*μ*-κ^2-*C,O*-$CH_2C(O)Me$}(*μ*-Cl)Cl-$(dmso)_2$], which we reported previously.[4] Thus, when **1** was reacted with py, Mepy, or ^tBupy in 1:1 molar ratio, complexes **3**−**5** were obtained along with 50% of unreacted **1**. $CDCl_3$ solutions of complexes **3**−**5** contain an approximately 10:1 mixture of trans and cis isomers. Complex **3** reacts with Tl(acac) in 1:1 molar ratio to give [Pd{$CH_2C(O)Me$}(acac)(py)] (**6**). Although complexes **2**−**6** are air stable, $CDCl_3$ solutions of **2**−**5** slowly decompose to give acetone and [$PdCl_2L_2$].

Synthesis of Cationic Complexes. The room-temperature reaction of complex **3** or **5** with TlOTf (1:1 molar ratio) in dry acetone gives almost instantly a precipitate of TlCl. From the filtrate, a mixture (by NMR) of products was isolated that we could not separate. However, bands corresponding to ν(CO) appearing at lower frequencies than in the starting complexes suggest the formation of some complex containing a bridging acetonyl or η^3-oxoallyl ligand.

Addition of L to the suspensions resulting from addition of TlOTf (1:1 molar ratio) in THF or acetone to complexes **3**−**5** led to the isolation of the corresponding cationic complexes [Pd{$CH_2C(O)Me$}L_3]TfO (L = py (**7**), Mepy (**8**), ^tBupy (**9**)). Alternatively, reaction of **1** with Mepy or ^tBupy and QTfO (Q = Tl, K, respectively) (1:3:1) also afforded complex **8** or **9**, respectively. The reaction of **9** with triphos (1:1 molar ratio) in THF gave [Pd{$CH_2C(O)Me$}(triphos)]TfO (**10**). We designed this reaction assuming that the P/C transphobia[23] induced a change of the acetonyl ligand to the enolato coordination mode. This has been observed in a few cases. Thus, although *cis*-[Pd(Ar)Br(dpb)] (Ar = C_6H_4Me-2, $C_6H_4{}^tBu$-4; dpb = 1,2-bis(diphenylphosphino)benzene) reacts with different potassium enolates KOC(=CRR′)R″ to give the expected 2-oxoalkyl complexes *cis*-[Pd(Ar){CRR′C(O)R″}(dpb)], when R = R′ = Me and R″′ = Ph, the enolato isomer *cis*-[Pd(Ar){OC(=CMe_2)C(O)Ph}(dpb)] was obtained.[22,24] The stabilization of the enolato isomer was attributed to steric reasons, which explains that in our case (R = R′ = H and R″ = Me) the ketonyl isomers **2** and **10** were obtained.

Reactions of 1 with Alkenes and Allenes. The reaction of **1** with norbornene (nbn, 1:2) was followed by ^1H NMR in CD_3CN. After 1 h, the reaction mixture showed the absence of complex **1**. When the reaction was repeated in a preparative scale in MeCN, a solid could be precipitated by addition of Et_2O. This solid could not be identified, but the presence of a band at 1714 cm^{-1} in the IR spectra suggested the insertion of the alkene into the Pd−$C_{acetonyl}$ bond. However, the reaction of **1** with norbornene followed by addition of bpy or dbbpy (1:2:

Scheme 2



1) led to [Pd{(nbn)$CH_2C(O)Me$}ClL_2] (L_2 = bpy (**11**), dbbpy (**12**)) (Scheme 2), although **12** could not be obtained analytically pure. Complex **11** results from the *syn* insertion of the *exo* face of the norbornene double bond into the Pd−$C_{acetonyl}$ bond. This is the general mode of insertion of this olefin into Pd−C bonds.[25] Only a limited number of examples of alkene insertion into a Pd−$C_{ketonyl}$ bond have been reported,[17,26] but **11** is the first such complex fully characterized. The behavior of **1** toward other olefins (cyclohexene, cyclooctene, maleic anhydride, and dimethyl maleate) was followed by ^1H NMR in CD_3CN, but no reaction was observed in any case after several days.

The reaction between **1** and 1,5-cyclooctadiene (cod; 1:1 molar ratio) in dry THF gave [PdCl{$CH_2C(O)Me$}(η^4-cod)] (**13**, Scheme 2). When the reaction was carried out in acetone, **13** was obtained contaminated with an impurity. The ^1H NMR spectrum in $CDCl_3$ solution of the crude product showed the presence of [$PdCl_2$(cod)], which could be the product of the

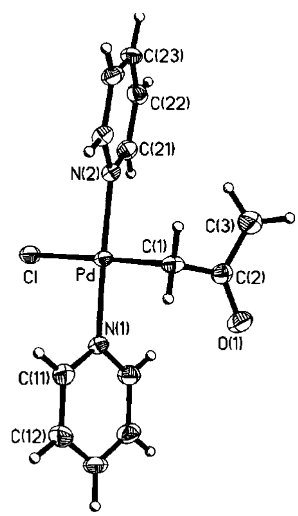


Figure 1. Ellipsoid representation of complex **3** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−N(2) = 2.0262(17), Pd−N(1) = 2.0270(17), Pd−C(1) 2.0804(19), Pd−Cl = 2.3869(5), O(1)−C(2) = 1.232(3), C(1)−C(2) = 1.460(3), C(2)−C(3) = 1.511(3), N(2)−Pd−C(1) = 90.03(7), N(1)−Pd−C(1) = 87.61(7), N(2)−Pd−Cl = 91.18(5), N(1)−Pd−Cl = 91.17(5), N(2)−Pd−N(1) = 177.61(6).

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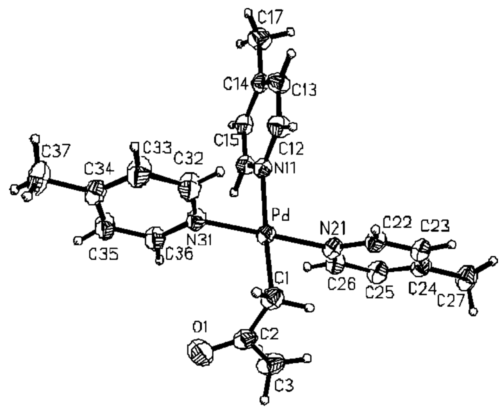

Figure 2. Ellipsoid representation of complex **8** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−N(31) = 2.0269(18), Pd−N(21) = 2.0328(18), Pd−C(1) = 2.056(2), Pd−N(11) = 2.1202(19), C(1)−C(2) = 1.464(4), O(1)−C(2) = 1.229(3), C(2)−C(3) = 1.512(3), N(31)−Pd−C(1) = 89.60(9), N(21)−Pd−C(1) = 90.56(9), N(31)−Pd−N(11) = 89.83(7), N(21)−Pd−N(11) = 89.96(7), C(2)−C(1)−Pd = 108.20(16), O(1)−C(2)−C(1) = 122.5(2), O(1)−C(2)−C(3) = 119.1(2), C(1)−C(2)−C(3) = 118.5(2).

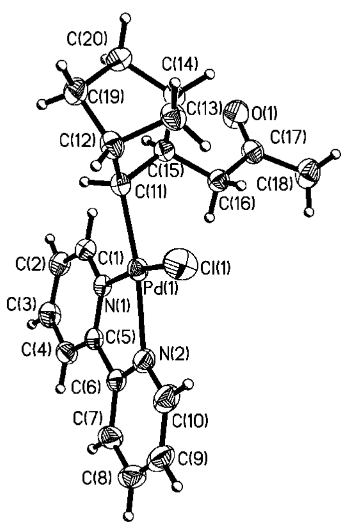

Figure 3. Ellipsoid representation of complex **11** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) = 2.043(2), Pd(1)−N(1) = 2.0753(17), Pd(1)−N(2) = 2.1518(18), Pd(1)−Cl(1) = 2.3069(12), O(1)−C(17) = 1.210(3), C(11)−C(12) = 1.544(3), C(11)−C(15) = 1.571(2), C(12)−C(13) = 1.536(3), C(12)−C(19) = 1.548(3), C(13)−C(14) = 1.530(3), C(14)−C(20) = 1.541(3), C(14)−C(15) = 1.550(3), C(15)−C(16) = 1.528(3), C(16)−C(17) = 1.510(3), C(17)−C(18) = 1.509(3), C(19)−C(20) = 1.554(3), C(11)−Pd(1)−N(1) = 93.56(7), N(1)−Pd(1)−N(2) = 78.42(6), C(11)−Pd(1)−Cl(1) = 94.36(6), N(2)−Pd(1)−Cl(1) = 93.51(5), C(12)−C(11)−C(15) = 103.09(14), C(13)−C(12)−C(11) = 102.64(15), C(13)−C(12)−C(19) = 100.61(17), C(11)−C(12)−C(19) = 107.15(17), C(14)−C(13)−C(12) = 94.74(16), C(13)−C(14)−C(20) = 102.22(17), C(13)−C(14)−C(15) = 101.85(15), C(20)−C(14)−C(15) = 107.97(16), C(16)−C(15)−C(14) = 111.82(15), C(16)−C(15)−C(11) = 115.50(15), C(14)−C(15)−C(11) = 102.45(14), C(17)−C(16)−C(15) = 114.15(16), O(1)−C(17)−C(18) = 120.55(19), O(1)−C(17)−C(16) = 122.22(18), C(18)−C(17)−C(16) = 117.22(18), C(12)−C(19)−C(20) = 103.54(16), C(14)−C(20)−C(19) = 102.70(17).

reaction between DCl (from $CDCl_3$) and an hydroxo complex (the impurity?) resulting from the hydrolysis of **13**. In addition, **13** slowly decomposes in chlorinated solvents to give [$PdCl_2$(cod)]. The reaction of **1** with norbornadiene (1:1 molar ratio) in dry THF gave a mixture of products that could not be separated.

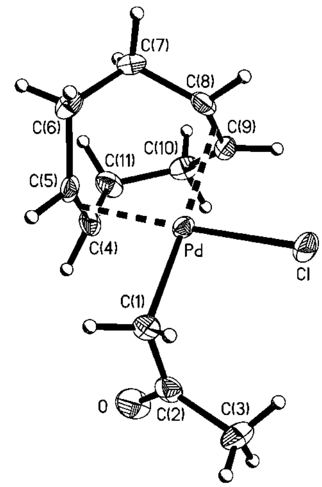

Figure 4. Ellipsoid representation of complex **13** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.072(3), Pd−C(5) = 2.178(3), Pd−C(4) = 2.193(3), Pd−Cl = 2.3268(9), Pd−C(9) = 2.329(3), Pd−C(8) = 2.358(3), O−C(2) = 1.225(4), C(1)−C(2) = 1.467(5), C(2)−C(3) = 1.501(5), C(4)−C(5) = 1.380(5), C(4)−C(11) = 1.520(4), C(5)−C(6) = 1.512(4), C(6)−C(7) = 1.525(5), C(7)−C(8) = 1.504(5), C(8)−C(9) = 1.354(5), C(9)−C(10) = 1.499(4), C(10)−C(11) = 1.539(5), C(1)−Pd−C(5) = 89.66(13), C(1)−Pd−C(4)= 92.41(13), C(5)−Pd−C(4) = 36.81(12), C(1)−Pd−Cl = 89.72(10), C(5)−Pd−C(9) = 94.95(12), C(4)−Pd−C(9) = 81.17(12), Cl−Pd−C(9) = 92.23(9), C(5)−Pd−C(8) = 80.17(12), C(4)−Pd−C(8) = 87.10(12), Cl−Pd−C(8) = 95.09(9), C(9)−Pd−C(8) = 33.58(11).

Addition of 1,1-dimethyl allene (dma) to a solution of **1** in acetonitrile (1.2:1 molar ratio) led to the isolation of the dinuclear π-allyl complex [Pd{η^3-$CH_2C[CH_2C(O)Me]CMe_2$}$_2$(μ-Cl)$_2$] (**14**, Scheme 2), resulting from the insertion of the allene into the Pd−C bond. The reaction of Me_4N[Pt{$CH_2C(O)Me$}Cl_2(η^2-C_2H_4)] with dma gives instead the substitution product *cis*-Me_4N[Pt{$CH_2C(O)Me$}Cl_2(η^2-H_2C=C=CMe_2)].[27]

Crystals apparently suitable for an X-ray crystallographic study were obtained for **14**, but although the structure shown in Scheme 2 was established, a complete crystallographic analysis was not possible. Disorder was so severe that, despite repeated attempts and data collection at low temperature, no satisfactory refinement was achieved. However, the composition and the position of the organic ligand acting as η^3-allyl were established with certainty. η^3-Allyl palladium complexes have

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Table 1. Crystallographic Data for Complexes

	3	8	11	13
formula	$C_{13}H_{15}ClN_2OPd$	$C_{22}H_{28}F_3N_3O_5Pd$ S	$C_{20}H_{23}ClN_2OPd$	$C_{11}H_{17}ClOPd$
fw	357.12	609.93	449.25	307.10
cryst habit	lath	block	block	block
cryst size (mm)	0.54 × 0.30 × 0.10	0.40 × 0.20 × 0.20	0.32 × 0.22 × 0.08	0.21 × 0.20 × 0.17
cryst system	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pbca*
cell constants				
a (Å)	8.2358(6)	14.0831(12)	7.956(5)	8.2836(8)
b (Å)	8.817(2)	11.5607(11)	9.980(5)	13.7315(7)
c (Å)	10.974(2)	16.9448(14)	12.514(5)	19.6036(11)
α (deg)	73.534(5)	90	97.255(5)	90
β (deg)	87.561(5)	112.467(4)	105.519(5)	90
γ (deg)	63.968(5)	90	103.746(5)	90
volume ($Å^3$)	683.6(2)	2549.4(4)	910.6(8)	2229.8(3)
Z	2	4	2	8
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (Mg m^{-3})	1.735	1.589	1.638	1.830
μ(Mo Kα) (mm^{-1})	1.541	0.869	1.176	1.868
F(000)	356	1240	456	1232
T (K)	173(2)	133(2)	100(2)	173(2)
$2\theta_{max}$ (deg)	50	60	52.7	50
no. of reflns measd	2523	39 875	10 018	3827
no. of indep reflns	2354	7461	3691	1962
transmissions	0.8611 and 0.4899	0.862 and 0.700	0.9118 and 0.7047	0.7418 and 0.6950
R_{int}	0.008	0.029	0.0143	0.0307
abs corr	psi-scans	semiempirical from equivalents	semiempirical from equivalents	psi-scans
no. restrnts/params	2354/136/164	560/386	0/227	88/128
$R_w(F^2$, all reflns)	0.0425	0.0910	0.0582	0.0446
$R(F, > 4\sigma(F))$	0.016	0.0320	0.0217	0.0232
S	1.07	1.049	1.13	0.84
max Δρ (e $Å^{-3}$)	0.32	1.11	0.33	0.40

been obtained by reacting alkyl,[20,28] aryl,[21] or acyl[28] palladium derivatives with allenes.

All attempts to react acetonitrile solutions of **1** with heterocumulenes (CS_2 and RN=C=S) or alkynes (diphenylacetylene and dimethyl acetilendicarboxylate) were unsuccessful, and the starting compounds or complex mixtures of products were obtained.

Crystal Structures. The crystal structures of complexes **3** (Figure 1), **8** (Figure 2), **11** (Figure 3), and **13** (Figure 4) have been solved. The palladium atoms are in an almost square-planar coordination. The decreasing trans influence of the ligands alkyl > acetonyl > olefin > chloro > pyridine ≈ bpy is shown by comparing the metal-to-donor atom bond distances. Thus, Pd−N bond distances trans to: py or bpy in **3** or **8** (2.0269(2)−2.0328(2) Å) < chloro in **11** (2.0753(17) Å) < acetonyl in **8** (2.1202(19) Å) < alkyl in **11** (2.1518(18) Å); Pd−C_{olefin} bond distances in **13** trans to: Cl (2.193(3), 2.178(3) Å) < acetonyl (2.358(3) and 2.329(3) Å); Pd−Cl bond distances trans to: bpy in **11** (2.3069(12) Å) < olefin in **13** (2.3268(9) Å) < acetonyl **3** (2.3869(6) Å); and Pd−CH_2 bond distances trans to: ^{t}Bupy in **8** (2.056(2) Å) < olefin in **13** (2.072(3) Å) ≈ chloro (2.0804(19) Å).

The structure of **11** shows the *exo* insertion of norbornene into the Pd−acetonyl bond. The C=O (1.210(3) Å) or CH_2−CO (1.510(3) Å) bond distance in **11** is slightly shorter or longer, respectively, than in **3** [1.232(3), 1.460(3) Å, respectively], **8** [1.229(3), 1.464(4) Å, respectively], or **13** [1.225(4), 1.467(5) Å, respectively]. In general, C=O and CH_2−CO bond distances in other acetonyl metal complexes are in the ranges 1.209(3)−1.232(5) and 1.475(4)−1.516(5), respectively.[2−5,7] The molecules of **11** associate in dimers through a $\pi\cdots\pi$ stacking of the bpy rings with a centroid−centroid distance of 3.450 Å.

Spectroscopic Properties. The ^{1}H NMR spectra of complexes show the methyl proton resonances in the wide range 1.21−2.53 ppm depending on neighboring group effects. Thus, in **10**, some of the aryl groups of the phosphine ligand cause the maximum shielding (1.21 ppm); in *trans*-**3**−**5** and **7**−**9**, the pyridine ligands lead to an intermediate shielding (1.72−1.78 ppm), while in *cis*-**3**, *cis*-**4**, **6**, and **11**−**14** the lower shielding is reached (2.07−2.53 ppm). The methylene acetonyl protons appear as singlets in the range 2.51−3.00 for complexes **3**−**9** and **13**. Those of complex **2** give a doublet of doublets at 2.70 ppm, and the $^{31}P\{^1H\}$ NMR spectrum consists of two doublets, in agreement with the proposed structure. For $CDCl_3$ solutions of complexes **3**−**5**, ^{1}H and ^{13}C NMR spectra, HMQC, and NOESY 2D experiments reveal they are 10−12:1 mixtures of trans/cis isomers. In the ^{1}H NMR spectra of complex **10**, the $CH_2C(O)$ protons appear as a doublet of triplets and the $^{31}P\{^1H\}$ NMR shows a triplet and a doublet for the P atoms trans and cis to the acetonyl ligand, respectively. The insertion of norbornene into the Pd−CH_2 bond to give complexes **11** and **12** causes the expected deshielding in only one of the methylene protons (3.45−3.47 ppm), while the other must be shielded by one of the bpy rings (2.83−2.89 ppm). In complex **14**, both methylene protons are, as expected, more deshielded (3.78, 3.26 ppm) than those in the acetonyl complexes.

The ^{1}H NMR spectrum of **11** shows the nonequivalence of the halves of the bpy ligand. ^{1}H NOESY 2D experiments reveal an interchange between both halves. A similar behavior has been found in other organopalladium complexes.[29,30] It has been

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proposed that it is due to a site exchange of the nitrogen donor atoms. The mechanism of this process involves Pd−N bond breaking and subsequent isomerization via a Y-shaped intermediate.[30] In **11**, the same mechanism could explain its fluxional behavior, although the intermediate could be a square-planar complex due to coordination of the carbonyl group. A similar behavior is found for complex **12**. The allyl moiety in **14** shows the *syn* and *anti* protons with a typical geminal coupling for this compound. NOESY 2D experiments reveal a NOE between the H *anti* and the Me *anti*. One $CH_2C(O)$ proton has a NOE with the Me *syn*, and the other one has a NOE with the H *syn*. This could be due to the rotational hindrance of the acetonyl group around the C−$CH_2C(O)$ bond.

One absorption is observed in the IR spectra of complexes **2**−**10** and **13**, in the region 1628−1650 cm^{-1}, corresponding to ν(C=O) in a terminal acetonyl ligand.[1–5] However, the absorption assignable to ν(C=O) in complexes **11**, **12**, and **14** appears where it is observed in organic ketones (1704−1714 cm^{-1}). The difference is in agreement with the shortening observed in the C=O distance in **11** with respect to those in **3** and **8** (see above).

The absorption frequency of the ν(Pd–Cl) band in the IR spectra of chloro complexes increases as the trans influence of the ligands decreases: acetonyl (**3**−**5**; 270−280 cm^{-1}) > P-donor ligand (**2**; 294 cm^{-1}) > N-donor ligand (**11**, **12**; 318 and 326 cm^{-1}), which is in accordance with the X-ray crystal structure data of **3** and **11** (see above). The ν(PdCl) band in **13** could not be assigned because several bands appear in the low-energy region. The bands at 240 and 260 cm^{-1} in **14** can be assigned to ν(PdCl) modes corresponding to bridging chloro ligands.

Conclusion

We report our final illustration of the synthetic capacity of the polymer $[Pd\{CH_2C(O)Me\}Cl]_n$ to prepare in good yields new types of acetonyl complexes: *trans*-$[Pd\{CH_2C(O)Me\}ClL_2]$, $[Pd\{CH_2C(O)Me\}L_3]^+$, and $[Pd\{CH_2C(O)Me\}$(*O,O*-acac)$L]^+$. Reactions with alkenes afford the adduct $[Pd\{CH_2C(O)Me\}$-Cl(cod)], the product resulting from the *syn* insertion of the *exo* face of the norbornene double bond into the Pd−$C_{acetonyl}$ bond, $[Pd\{(nbn)CH_2C(O)Me\}ClL_2]$, which is the first such complex fully characterized, or the π-allyl complex $[Pd\{\eta^3$-CH_2C-$[CH_2C(O)Me]CMe_2\}_2(\mu$-$Cl)_2]$ resulting from the insertion of 1,1-dimethyl allene in the Pd−$C_{acetonyl}$ bond.

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Supporting Information Available: CIF files, listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond length and angles for complexes **3**, **8**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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