Stepwise Ethene and/or Methyl Acrylate/CO Insertions into the Pd–C Bond of Cationic Palladium(II) Complexes Stabilized by a (P,O) Chelate**

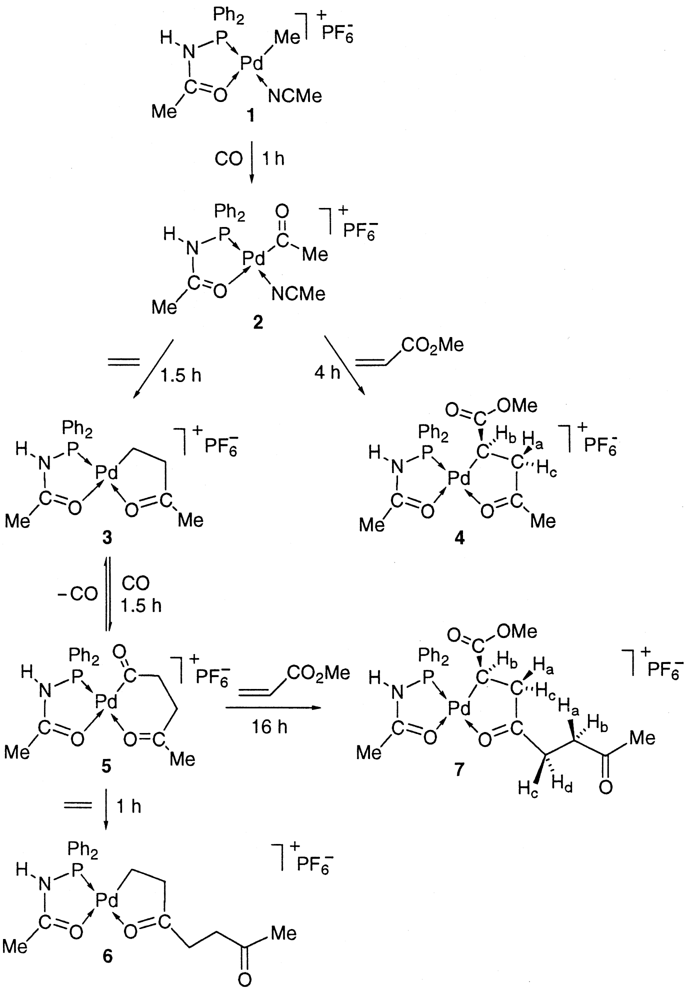
Pierre Braunstein,* Céline Frison,* and Xavier Morise*

Dedicated to Professor R. Guilard
on the occasion of his 60th birthday

The palladium-catalyzed alternating copolymerization of olefins and CO has become a major field of research in academic and industrial laboratories.[1–4] This is because of the possibility of fine-tuning the reaction at the molecular level, the low cost of the monomers, and the properties, applications, and possible subsequent functionalization of the resulting polyketones.[5–8] Theoretical and experimental studies have established the kinetic and thermodynamic factors controlling the chain-growth mechanism, which consists of alternating CO and olefin migratory insertion into the metal–alkyl and the metal–acyl bond, respectively.[1–3, 9–13] However, owing to difficulties encountered in the isolation of intermediates, detailed investigations on the early stages of the chain-growth process have been carried out mainly with strained alkenes and to date only one structural report on ethene–CO coupling has been published.[14] Furthermore, there is considerable interest in the copolymerization of olefins with polar monomers, such as methyl acrylate. However, despite recent achievements,[15] the need to increase the percentage of functional groups in the final copolymers remains. To do this requires methods that enhance the relative rates of insertion of the polar monomer into the growing chain.

Here we present results obtained with Pd^{II} complexes in which the acetamido-derived ligand $Ph_2PNHC(O)Me$ acts as a dissymmetric P,O chelate. These complexes have enabled us to 1) isolate and structurally characterize the metallacyclic complex resulting from the first CO–ethene coupling step, 2) isolate a complex obtained after insertions of CO and methyl acrylate into a Pd–Me bond, and 3) prepare complexes resulting from successive CO, ethene, CO, and then either incorporation of an ethene or methyl acrylate molecule.

When a dichloromethane solution of complex **1** (P,O = $Ph_2PNHC(O)Me$) was exposed to 1 atm of CO, the acyl complex **2** was formed quantitatively (Scheme 1) as evidenced by a ν(CO) vibration at 1716 cm^{-1} in the IR spectrum and a resonance at $\delta = 217.0$ in the ^{13}C NMR spectrum. This resonance has a small $^2J(P,C)$ coupling of 4 Hz which indicates that the acyl group in **2** resides in a *cis* position relative to the phosphorus atom just like the methyl ligand in **1**.[10, 16, 17] Further corroboration comes from the large high-field shift ($\Delta\delta = -20.4$) of the ^{31}P NMR resonance of **2** ($\delta = 58.9$), compared to **1** ($\delta = 79.3$), formation of a *trans* isomer would cause a smaller shift (ca. −10 ppm).[18, 19] Owing to the *cis* nature of the migratory insertion of CO into palladium–carbon bonds,[3, 13, 18, 20–22] an isomerization process, either before or after formation of the acyl ligand, must occur during the formation of **2** which appears to be the thermodynamic isomer. The preference for a soft carbon ligand (either alkyl or acyl) to avoid a position *trans* to a phosphorus atom is consistent with Pearson's antisymbiotic effect.[23] Complex **2** shows a remarkable stability towards decarbonylation and/or decomposition, both in solution and in the solid state. This result contrasts with the majority of known cationic acylpalladium complexes, which rapidly decompose, even in the solid state, and are therefore rarely isolated.[2, 9, 11, 12, 17, 21, 24]



Scheme 1. All reactions performed at RT in CH_2Cl_2.

Insertion of ethene into the palladium–acyl bond of **2** occurred at ambient temperature under atmospheric pressure. The reaction was completed after approximately 90 minutes ($^{31}P\{^1H\}$ NMR monitoring) and afforded complex **3**

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

(Scheme 1). Coordination of the ketonic oxygen atom to the Pd center ($\tilde{\nu}_{CO} = 1635$ cm^{-1}) forms a stabilizing chelate which makes β-hydrogen elimination less likely.[25, 26] In fact **3** is stable at ambient temperature for several hours in solution and for days in the solid state, in contrast to diphosphane (P,P) complexes of the type [Pd{CH$_2$CH$_2$C(O)Me}(P,P)].[9] This observation illustrates the beneficial role of our P,O ligand. The ^{31}P{^{1}H} NMR signal of **3** ($\delta = 77.4$) is shifted to low field relative to that of **2**. In the ^{1}H NMR spectrum of **3** the methylene protons give rise to two triplets at $\delta = 2.11$ (Pd–CH$_2$) and 3.24 (CH$_2$C=O). Related metallacycles have been isolated upon insertion of propene,[2, 10] styrene,[2, 27, 28] and cyclic mono-[11, 24, 29–33] and diolefins[2, 11, 12, 18, 31–35] into palladium–acyl bonds. For ethene, however, there are few precedents,[3, 9, 14, 35] and **3** represents the first complex of this type containing a P,O ligand. Many such heterobidentate P,O ligands play key roles in homogeneous catalysis, including the nickel-catalyzed ethene oligomerization to linear α-olefins in which minor changes are known to have considerable chemical consequences.[36, 37] The structure of **3** was unambiguously determined by X-ray diffraction (Figure 1) and is only the second ethene–acyl coupling product to be so characterized.[14] Even with other olefins, very little structural data is available.[11, 38] Our structure confirms the presence of the C,O and P,O chelates, with a *cis* arrangement of the two carbonyl moieties (O(1)-Pd-O(2) 101.66°). The Pd–O(1) bond (2.141(2) Å) is longer than in related norbornene–CO coupling products (2.016(5)–2.033(5) Å).[11] The Pd–C(1) bond length in the five-membered ring (2.002(3) Å) is comparable to those of Pd-bound sp^3-carbon atoms *trans* to a carbonyl oxygen atom.[21, 38–40]

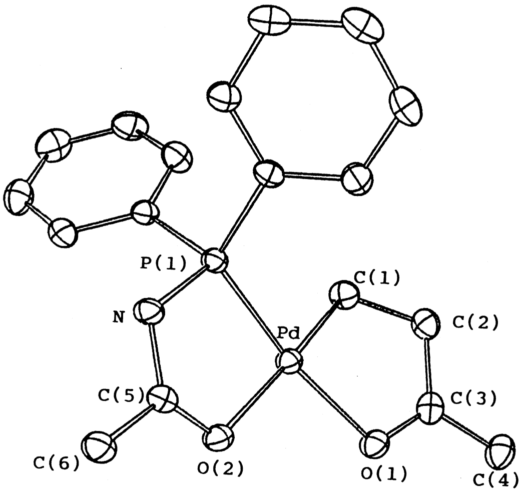

Figure 1. Molecular structure of the cation [Pd{CCH$_2$CH$_2$C(O)OCH$_3$}(P,O)]$^+$ in **3** (H atoms not shown). Selected bond lengths [Å] and angles [°]: Pd-C(1) 2.002(3), Pd-O(1) 2.141(2), Pd-O(2) 2.176 (2), Pd-P 2.1719(8), C(1)-C(2) 1.530 (5), C(3)-O(1) 1.237(4), O(2)-C(5) 1.233(4), C(5)-N 1.359(4), N-P 1.709(3); O(1)-Pd-C(1) 80.8(1), C(1)-Pd-O(2) 177.4(1), O(1)-Pd-P(1) 170.95(7), O(1)-Pd-O(2) 101.66(8), P-N-C(5) 119.5(2), N-C(5)-O(2) 121.9(3).

When complex **2** was treated with methyl acrylate, ^{31}P{^{1}H} NMR monitoring revealed the complete disappearance of **2** after approximately 4 h at ambient temperature. A new resonance appeared at $\delta = 81.9$, the same region as that of **3**. The ^{1}H NMR spectrum of the new complex **4** (Scheme 1) in [D$_6$]acetone contains three methyl signals at $\delta = 2.45$, 2.61 (Me-C(O)), and 2.91 (OMe), whereas the CH and CH$_2$ protons H$_a$, H$_b$, and H$_c$ resonate at $\delta = 3.16$, 3.22, and 3.44, respectively. The values for the vicinal and geminal J(H,H) as well as the J(P,H) couplings (see Experimental Section) are consistent with a five-membered C,O chelate in **4**. The ν(CO) vibration, assigned to the ester group at 1692 cm^{-1} (compared to 1744 cm^{-1} in EtC(O)OMe and 1731 cm^{-1} in methyl acrylate), reflects the presence of the palladium in the position α to the C(O)OMe group.[41]

Interestingly, the stability of the C,O chelate in **3** did not prevent the facile CO insertion into the Pd–C bond to give the α-keto chelate **5** (Scheme 1), as evidenced by a new ν(CO) vibration at 1708 cm^{-1} and a ^{31}P{^{1}H} NMR resonance ($\delta = 63.0$) in the same region as that of the acyl complex **2**. This carbonylation reaction is, however, easily reversible. The signals assigned to the methylene protons have drawn closer together ($\delta = 2.66$ and 2.84) compared with **3**. Whereas Brookhart et al. have described the formation of such a six-membered chelate in a 1,10-phenanthroline palladium complex,[3] CO insertion into other PdCH$_2$CH$_2$C(O)Me systems either did not occur[35] or led to a nonchelating C(O)CH$_2$CH$_2$-C(O)Me chain.[9, 14, 17]

The six-membered metallacycle in **5** inserted ethene under ambient conditions to afford complex **6** (Scheme 1). Its spectroscopic data resemble those for **3**, but with additional characteristic signals for a pendant ketone chain. Here again, the ketonic oxygen atom of the chelate is *trans* to the phosphorus atom. Complex **5** was also treated with methyl acrylate (under a CO atmosphere to avoid decarbonylation to **3**) and insertion into the Pd–C(O) bond occurred after 16 h at ambient temperature (^{31}P{^{1}H} NMR monitoring). This afforded complex **7** as the sole product in 75 % yield (Scheme 1). This yellow complex was fully characterized by spectroscopic methods (see Supporting Information). The ν(CO) vibrations at 1631 and 1601 cm^{-1} are assigned to the coordinated C=O groups of the five-membered chelates C,O and P,O, respectively. Two other absorptions at 1714 and 1700 cm^{-1} are assigned to the pendant keto group of the growing chain and to the ester function of the acrylate, respectively. Like **4**, complex **7** does not react with CO under ambient conditions, which may be the result of a stronger Pd–C bond than in **3**.

The use of a dissymmetric P,O ligand in this chemistry offers the advantage over symmetrical P,P or N,N ligands of orientating the *trans* ligands in a more selective manner. Catalytic investigations are currently being performed to see if terpolymerization is achievable.

Experimental Section

Reactions were carried out under inert atmosphere in purified solvents. All compounds gave satisfactory elemental analyses. Full details are given in the Supporting Information.

Selected data: **1**: Solid [PdCl(Me)(cod)] (cod = 1,5-cyclooctadiene)[42] (1.086 g, 4.098 mmol) was added to a solution of Ph$_2$PNHC(O)Me (1.004 g, 4.098 mmol) in MeCN (300 mL) followed by addition of TlPF$_6$ (1.432 g, 4.098 mmol). The solution was stirred for 30 min, filtered and the solvent evaporated. The residue was washed with diethylether (25 mL) and dried in vacuo to afford **1** as a white solid (2.030 g, 90 % yield). IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1614$s cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta=0.76$ (d, ^3J(P,H) = 1.8 Hz, 3H; Pd-CH_3), 2.22 (s, 3H; CH_3), 2.25 (s, 3H; CH_3), 8.40 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): $\delta=-4.0$ (s; Pd-CH_3), 3.0 (s, CH_3CN), 22.4 [s; NC(O)CH_3], 119.4 (s; C≡N), 182.9 (d, ^{2+3}J(P,C) = 5 Hz; CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta=79.3$.

2: CO was bubbled through a solution of **1** (0.500 g, 0.908 mmol) in CH_2Cl_2 (70 mL) at room temperature for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with pentane (20 mL) and dried in vacuo, to afford **2** as a yellow powder (0.464 g, 88 % yield). This complex can be stored for weeks in a Schlenk flask under an atmosphere of N_2 and in CH_2Cl_2 no decomposition was observed after 1 week. IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1716$s, 1618s cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta=2.30$ (d, ^4J(P,H) = 1.5 Hz, 3H; Pd-C(O)CH_3), 2.32 (s, 3H; CH_3CN), 2.35 (d, ^4J(P,H) = 1.2 Hz, 3H; NC(O)CH_3), 10.00 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (50 MHz, CD_3CN): $\delta=23.3$ (s; NC(O)CH_3), 37.0 (d, ^3J(P,C) = 26 Hz; PdC(O)CH_3), 182.5 (d, ^{2+3}J(P,C) = 4 Hz; NC(O)CH_3), 217.0 (d, ^2J(P,C) = 4 Hz; PdC(O)CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone): $\delta=58.9$.

3: C_2H_4 was bubbled through a solution of **2** (0.245 g, 0.422 mmol) in CH_2Cl_2 (30 mL) at room temperature for 1.5 h. The workup as described for **2**, afforded **3** as an orange powder (0.180 g, 75 % yield). Yellow crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/pentane. IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1635$m, 1611m cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta=2.11$ (t, ^3J(H,H) = 6.1 Hz, 2H; PdCH_2), 2.44 (s, 3H; CH_3), 2.52 (s, 3H; CH_3), 3.24 (t, ^3J(H,H) = 6.1 Hz, 2H; PdCH$_2$CH_2), 10.37 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta=18.1$ (s, PdCH_2), 22.3 (d, ^3J(P,C) = 4.2 Hz; NC(O)CH_3), 28.2 (d, ^4J(P,C) = 2.2 Hz; CH_2C(O)CH_3), 51.03 (s; PdCH$_2$CH_2), 183.8 (d, ^{2+3}J(P,C) = 4.9 Hz; NC(O)CH_3), 234.4 (d, ^3J(P,C) = 1.9 Hz; CH_2C(O)CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone): $\delta=77.4$.

4: Methyl acrylate (1.64 equiv, 139.0 µL, 1.542 mmol) was added to a solution of **2** (0.545 g, 0.940 mmol) in CH_2Cl_2 (70 mL). The solution was stirred for 4 h at ambient temperature to give a yellow solution. After filtration and removal of the volatiles under vacuum, the yellow residue was washed with pentane (2 × 20 mL) and dried in vacuo to afford **4** (0.490 g, 83 % yield). IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1692$m, 1632m, 1601m cm^{-1}; ^{1}H NMR (500 MHz, [D$_6$]acetone): 2D NMR experiments (COSY, HMBC, HSQC) and simulation with the program gNMR were used to determine the chemical shifts and coupling constant of the complex spin systems formed by the $CHCH_2$ protons and to distinguish the different methylene groups; $\delta=2.45$ (d, ^4J(P,H) = 0.6 Hz, 3H; NC(O)CH_3), 2.61 (s, 3H; CH_2C(O)CH_3), 2.91 (s, 3H; OCH_3), ABCX (X = P) system for Pd-CH_b-CH_aH_c: 3.16 (ddd, $^2J(H_c,H_a)=19.3$, $^3J(H_a,H_b)=2.4$, ^4J(P,H) = 0.6 Hz, 1H; H_a), 3.22 (ddd, $^3J(H_c,H_b)=6.1$, $^3J(H_a,H_b)=2.4$, ^3J(P,H) = 2.3 Hz, 1H; H_b), 3.44 (dd, $^2J(H_c,H_a)=19.3$, $^3J(H_c,H_b)=6.1$ Hz, 1H; H_c), 9.20 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (125 MHz, [D$_6$]acetone): $\delta=22.0$ (d, ^3J(P,C) = 4.1 Hz, NC(O)CH_3], 28.3 (s, CH_2C(O)CH_3), 33.2 (s, PdCH), 51.3 (s, C(O)OCH_3), 51.8 (s, PdCHCH_2), 176.5 (s, C(O)OCH_3), 185.8 (d, ^2J(P,C) = 4.2 Hz, NC(O)CH_3), 235.8 (d, ^3J(P,C) = 2.5 Hz, CH_2C(O)CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz,[D$_6$]acetone): $\delta=81.9$.

5: Complex **5** was obtained in a similar manner to **2** from a CO purged solution of **3** (1.800 g, 3.186 mmol) in CH_2Cl_2 (100 mL) as a yellow powder (1.509 g, 79 % yield). IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1708$s, 1657m, 1616m cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=2.30$ (d, ^4J(P,H) = 1.0 Hz 3H; NHC(O)CH_3), 2.48 (s, 3H; CH_2C(O)CH_3), 2.66 (t, ^3J(H,H) = 6.0 Hz, 2H; PdC(O)CH_2), 2.84 (t, ^3J(H,H) = 6.0 Hz, 2H; CH_2C(O)CH_3), 8.65 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta=23.1$ (d, ^3J(P,C) = 4.2 Hz, NC(O)CH_3), 31.1 (d, ^4J(P,C) = 1.9 Hz, CH_2C(O)CH_3), 38.0 (s, CH_2C(O)CH_3), 39.2 (d, ^3J(P,C) = 24.6 Hz, PdC(O)CH_2), 183.5 (d, ^{2+3}J(P,C) = 5.4 Hz, NC(O)CH_3), 214.3 (d, ^2J(P,C) = 8.8 Hz, PdC(O)), 219.6 (s, Pd(O)CCH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone): $\delta=63.0$.

6: Complex **6** was obtained in a similar manner to **3** from a C_2H_4-purged solution of **5** (0.050 g, 0.084 mmol) in CH_2Cl_2 (15 mL) after 1 h as a yellow powder (0.036 g, 69 % yield). IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1715$m, 1630m, 1613s cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=1.76$ (dt, ^3J(H,H) = 6.0, ^3J(P,H) = 2.0 Hz, 2H; PdCH_2), 1.92 (s, 3H; CH_2C(O)CH_3), 2.08 (d, ^4J(P,H) = 0.5 Hz, 3H; NHC(O)CH_3), 2.65 (m, 4H; CH_2CH_2C(O)CH_3), 2.84 (dt, ^3J(H,H) = 6.0, ^4J(P,H) = 0.5 Hz, 2H; PdCH$_2$CH_2), 8.81 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta=18.4$ (s; PdCH_2CH$_2$), 22.3 (d, ^3J(P,C) = 4.2 Hz; NC(O)CH_3), 29.5 (s; CH_2C(O)CH_3), 34.5 and 38.3 (2 × s; C(O)$CH_2$$CH_2$C(O)), 50.4 (s; PdCH$_2$$CH_2$), 183.8 (d, ^2J(P,C) = 4.8 Hz; NC(O)CH_3), 206.6 (s; CH_2C(O)CH_3), 235.0 (s; CH_2C(O)CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone): $\delta=77.5$.

7: Complex **7** was prepared from **5** (0.780 g, 1.311 mmol) and 1.2 equiv of methyl acrylate (141 µL, 1.573 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was stirred at ambient temperature for 16 h under an atmosphere of CO. The solution was then filtered, and the volatiles were removed under vacuum to leave a yellow powder (0.670 g, 75 % yield). IR (CH_2Cl_2): $\tilde{\nu}_{CO}=1714$s, 1700s, 1631m, 1601s cm^{-1}; ^{1}H NMR (500 MHz, [D$_6$]acetone): 2D NMR experiments (COSY, HMBC, HSQC) and simulation with the program gNMR were used to determine the chemical shifts and coupling constants of the complex spin systems formed by the $CHCH_2$ and CH_2CH_2 protons and to distinguish the different methylene groups; $\delta=2.19$ (s, 3H; CH_2C(O)CH_3), 2.44 (s, 3H; NC(O)CH_3), 2.92 (s, 3H; OMe), ABCD spin system for C(O)$CH_cH_dCH_aH_b$C(O)CH_3: 2.96 (ddd, $^2J(H_a,H_b)=20.3$, $^3J(H_a,H_c)=7.0$, $^3J(H_a,H_d)=5.2$ Hz, 1H; H_a), 3.00 (ddd, $^2J(H_a,H_b)=20.3$, $^3J(H_b,H_c)=4.7$, $^3J(H_b,H_d)=7.7$ Hz, 1H; H_b), 3.10 (ddd, $^3J(H_c,H_a)=7.0$, $^3J(H_c,H_b)=4.7$, $^2J(H_c,H_d)=18.5$ Hz, 1H; H_c), 3.20 (ddd, $^2J(H_d,H_c)=18.5$, $^3J(H_d,H_b)=7.7$, $^3J(H_d,H_a)=5.2$ Hz, 1H; H_d), ABCX (X = P) spin system for Pd-CH_b-CH_aH_c: 3.20 (dd, $^2J(H_c,H_a)=19.0$, $^3J(H_a,H_b)=2.6$ Hz, 1H; H_a), 3.24 (ddd, $^3J(H_c,H_b)=6.0$, $^3J(H_a,H_b)=2.6$, ^3J(P,H) = 2.0 Hz, 1H; H_b), 3.42 (dd, $^3J(H_c,H_b)=6.0$, $^2J(H_c,H_a)=19.0$ Hz, 1H; H_c), 10.54 (brs, 1H; NH); $^{13}C\{^1H\}$ NMR (125 MHz, [D$_6$]acetone): $\delta=21.7$ (d, ^3J(P,C) = 4.8 Hz, NC(O)CH_3), 29.6 (s, CH_2C(O)CH_3), 33.0 (s, PdCH), 35.4 (d, ^4J(P,C) = 1.9 Hz, $CH_2$$CH_2$C(O)$CH_3$), 37.7 (s, CH_2C(O)CH_3), 50.9 (s, PdCHCH_2), 51.2 (s, C(O)OCH_3), 176.2 (s, C(O)OCH_3), 185.6 (d, ^{2+3}J(P,C) = 3.8 Hz, NC(O)CH_3), 210.0 (s, CH_2C(O)CH_3), 236.3 (d, ^3J(P,C) = 1.9 Hz, CH_2C(O)CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz,[D$_6$]acetone): $\delta=81.6$; FAB-MS: m/z: 534 (27 %) [M^+].

Crystallographic data for **3**: $C_{18}H_{21}F_6NO_2P_2Pd$; $M_r=565.71$, monoclinic, space group $P2_1/n$, $a=8.6887(2)$, $b=18.822(1)$, $c=13.0904(6)$ Å, $\beta=100.983(3)^\circ$, $V=2101.6(3)$ Å^3, $Z=4$, $\rho_{calcd}=1.79$ g cm^{-3}, $\mu=1.103$ mm^{-1}, $F(000)=1128$, $\lambda(Mo_{K\alpha})=0.71073$ Å, $T=173$ K. Red crystal, dimensions $0.20\times0.15\times0.15$ mm^3. A total of 12017 reflections were collected on a Kappa CCD diffractometer (ϕ scans, $2<\theta<29^\circ$). The structure was solved using direct methods and refined against $|F|$. Absorption corrections were computed from the psi scans of four reflections. For all computations the Nonius MoLEN package[43] was used: $R=0.041$, $Rw=0.059$, GOF = 1.049, maximum residual electron density 0.801 e Å^{-3} for 4413 reflections having $I>3\sigma(I)$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced as fixed contributors ($d_{C-H}=0.95$ Å, $B(H)=1.3B_{eq}(C)$ Å^2). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136484. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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An Efficient, Modular Synthetic Route to Oligomers Based on Zirconocene Coupling: Properties for Phenylene – Thiophene-1-Oxide and Phenylene – Thiophene-1,1-Dioxide Chains[**]

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The increasing interest in π-conjugated polymers has resulted in a very large research effort, focused on the development of new conducting materials for electronic devices.[1] Associated with this effort has been the synthesis and study of conjugated oligomers with well-defined structures and properties.[2] Oligomeric species allow detailed investigations of the fundamental properties of conjugated chains, and provide insight into the behavior of the analogous polymers. In addition, the discrete properties of the oligomers make them attractive materials in their own right, since they may exhibit properties that are not associated with the related polymers.

We have developed a new route to conjugated polymers based on the zirconocene coupling of diynes.[3, 4] This approach provides synthetic intermediate polymers containing zirconacyclopentadiene units, which are readily converted into a variety of new structures. These chemical transformations provide a modular approach to control the electronic and optical properties of the polymer, through substitution at a particular site in the conjugated chain by various structural units (for example dienylene, phenylene, thiophene, selenophene, germole, and phosphole). Related strategies which complement this approach involve the zirconocene coupling of functionalized diynes, to provide new monomers for polymerization[3f, 4] and the incorporation of zirconacyclopentadiene units by the coupling of diyne segments in a preexisting polymer.[3b,c,g]

A recent discovery in our laboratories[4] allows the efficient incorporation of thiophene-1-oxide (T_O) and thiophene-1,1-dioxide (T_{O2}) rings into the backbone of a conjugated polymer by the reaction of zirconacyclopentadiene derivatives with SO_2. Thus, we have been able to prepare the first polymers containing T_O groups and develop general routes to alternating arylene – T_O and arylene – T_{O2} copolymers.[3g] Interestingly, these polymers have more narrow band gaps, and have higher electron affinities than the corresponding thiophene-based polymers. In related work based on a different synthetic strategy, Barbarella et al. have shown that T_{O2} groups may be incorporated into oligomers which exhibit decreased electronic band gaps and higher electron affinities than the

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