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Synthesis and Molecular Structure of $[\overline{\mathrm{Pd\{CH_2CH_2C(O}})\mathrm{Me\}(HL)][BAr'_4]}$ (HL = 6-Me-2,2′-bipyridine, Ar′ = 3,5-$(CF_3)_2C_6H_3$), an Intermediate Relevant to Ethene/CO Copolymerization

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Summary: In the ethene/CO copolymerization catalyzed by palladium derivatives, species arising from ethene insertion into the palladium−acyl bond have been shown to play a key role. We report here the synthesis, spectroscopic characterization, and X-ray structure of the complex $[\overline{\mathrm{Pd\{CH_2CH_2C(O}})\mathrm{Me\}(HL)][BAr'_4]}$ *(HL = 6-Me-2,2′-bipyridine, Ar′ = 3,5-$(CF_3)_2C_6H_3$),* ***4****, the first one having an ancillary N,N ligand to be characterized in the solid state.*

Olefin insertion into a Pd−acyl bond is assumed to be a crucial step in the palladium-catalyzed copolymerization of carbon monoxide and alkenes.[1] The insertion product is generally a complex of the type $[(L)_2Pd\{CHRCHR'C(O)R''\}]^+$: the intramolecular coordination of the carbonyl oxygen to palladium likely gives a significant contribution to the stability of these intermediates. Evidence for species of this type has been achieved mostly by spectroscopic techniques. Some of them have been isolated in the solid state: they usually contain strong chelating ligands (N,N; P,P; N,P) and concern insertion of strained or bulky alkenes.[2] At variance, in the case of ethene insertion, only a few species have been isolated and shown to be stable in the solid state even at room temperature.[3] The crystal structure of the complex $[\overline{\mathrm{Pd\{CH_2CH_2C(O}})\mathrm{Me\}(NC_6H_4\text{-}COOMe\text{-}2)(PPh_3)][BF_4]}$ has been solved by X-ray diffraction.[4] The structure shows that, in addition to the coordination of the five-membered C,O ring, of the phosphorus atom, and of the nitrogen of the pyridine ring, the stability is enhanced by a long-range interaction involving the oxygen atom of the hybrid N,O ligand, positioned in axial position. Very recently the structures of two mononuclear species with a P,O[5] and a P,N[6] ancillary ligand, as well as that of a heterobimetallic derivative, $[(OC)_4\overline{\mathrm{Fe}(\mu\text{-}\mathrm{Ph_2PNHPPh_2})\mathrm{P}}\overline{\mathrm{d\{CH_2CH_2C(O}})\text{-}\mathrm{Me\}][BF_4]}$,[7] have been solved. This prompted us to report that in the course of a study on the catalytic activity in CO/ethene copolymerization of palladium(II) derivatives with 6-substituted-2,2′-bipyridines we have been able to isolate complex **4** according to the reaction Scheme 1 and to grow crystals suitable for X-ray diffraction.

All three steps depicted in Scheme 1 occur under mild conditions, i.e., at room temperature and atmospheric pressure. The second step is likely to be dictated by the insolubility of NaCl in dichloromethane and by the absence of potential donors, either as solvents or anions. Complexes **1** and **2** have been isolated and fully characterized, whereas **3** was detected only in solution.[8] Complex **3** and the last step in Scheme 1 are the same described by Brookhart in the case of the analogous

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(8) Selected IR and NMR data for **3**: IR (CH_2Cl_2, ν_{max}/cm^{-1}) 2118; ^{1}H NMR (CD_2Cl_2) δ 1.57 (s, 3H, Pd-Me), 2.85 (s, 3H, bipy-6-Me), 7.58−8.20 (6H, aromatics), 8.62 (d, 1H, H6′). We did not attempt to isolate **3** at low temperature.

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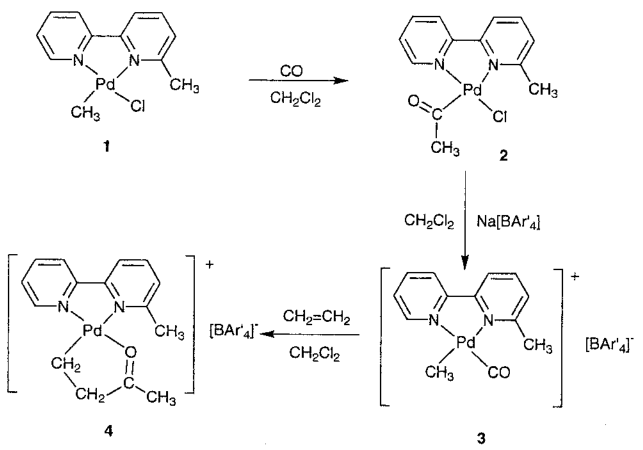
Scheme 1



derivative with 1,10-phenantroline (phen).[3a,b] Of the two possible geometric isomers, only one is formed for complexes **1**−**4**. For **1** and **2** evidence for the isomer having the chloride in proximity of the methyl substituent is given by the ^{1}H NMR spectrum. The assessment relies on the chemical shift of the H6′ proton which is known to be remarkably influenced by the neighboring ligands. The values observed for **1** and **2** indicate that the methyl group is close to H6′. It is worth noting that the formation of the same isomer has been recently described for a series of analogous methyl chloride derivatives of platinum(II) with 6-alkyl-substituted-2,2′-bipyridines.[9] Several factors have been considered to interpret the stereoselectivity observed, the most likely being the H bond formed between H−C(α) of the substituent and the chloride ion bound to the Pt center.

Evidence for the intermediate **3** rests on the IR spectrum, which shows a strong absorption in the region of a terminal carbonyl (ν(CO) = 2118 cm^{-1}) as well as upon an NMR NOE difference experiment.[10]

Complex **4** exhibits in the IR spectrum a strong ν(CO) absorption at 1615 cm^{-1} (CH_2Cl_2), supporting coordination of the carbonyl group.[2a,c] In the ^{1}H NMR spectrum the methylene protons appear as two triplets at δ 2.44 (CH_2-Pd) and δ 2.75 (CH_2CO). A NOESY spectrum[11] helped in the assignments and established that the CH_2 group bound to palladium is close to the bipy H6′ proton.[12] In the $^{13}C\{^{1}H\}$ spectrum the resonances at δ 25.04 and 49.54 can be ascribed to Pd-*C*H$_2$ and Pd-CH$_2$-*C*H$_2$, respectively, the latter being shifted downfield owing to the proximity of the carbonyl group. The carbon resonance of the C(O) group is observed at δ 238.95, significantly shifted with respect to organic ketones.[2f,g]

The crystal structure of compound **4** confirms that the preferred isomer has the σ Pd−C bond *trans* to the nitrogen atom of the substituted pyridine. An ORTEP view of the cation is shown in Figure 1. Selected bond lengths and angles are listed in the Figure 1 caption. The metal atom is in a square planar coordination with a very slight tetrahedral distortion. The Pd−O and Pd−C12 lengths can be compared with corresponding interactions in the recently reported cation [Pd{CH$_2$-CH$_2$C(O)Me}(P,O)]$^{+}$ (P,O = Ph$_2$PNHC(O)Me), compound **5**.[5] The Pd−O distance found here, 2.069(2) Å, is shorter than that found in **5**, 2.141(2) Å; the latter is however elongated by the influence of the *trans* phosphorus atom. The Pd−C distance, 2.046(4) Å, is longer than in **5**, 2.002(3) Å, thus suggesting that the *trans*-influence of nitrogen is slightly larger than that of oxygen. The Pd−N2 bond, 2.198(3) Å, is rather long, even when considering the influence of the *trans* alkyl group: compare for instance Pd−N = 2.146(2) Å in [Pd(L^{tb})Cl], HL^{tb} = $N_2C_{10}H_7CMe_3$, and Pd−N = 2.138(2) Å in [Pd(L^{np})Cl], HL^{np} = $N_2C_{10}H_7CH_2CMe_3$, compound **6**.[13] The Pd−N1 distance, 2.022(2) Å, is normal; see for instance Pd−N = 2.046(2) Å in compound **6**, Pt−N = 2.013(2) Å in [Pt(HL^{Et})(Me)(MeCN)]$^{+}$, HL^{Et} = $N_2C_{10}H_7Et$, and Pt−N = 2.022(4) Å in [Pt(HL^{Et})-(Me)Cl].[9]

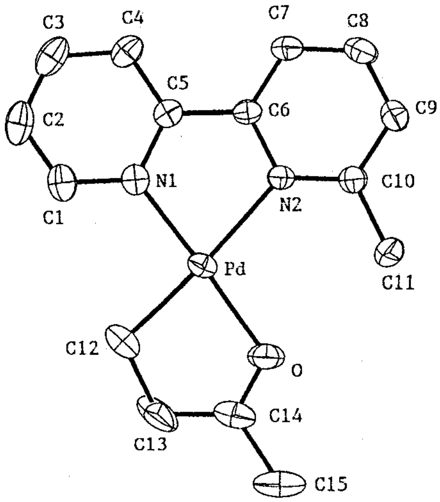


Figure 1. ORTEP view of the cation in compound **4**. Ellipsoids are drawn at the 30% probability level. Principal bond (Å) and angle (deg) parameters: Pd−O 2.069(2), Pd−N1 2.022(2), Pd−N2 2.198(3), Pd−C12 2.046(4), C12−C13 1.525(5), C13−C14 1.459(5), C14−O 1.241(5), C14−C15 1.536(4), O−Pd−N1 177.3(1), O−Pd−N2 102.9(1), O−Pd−C12 81.8(1), N1−Pd−N2 79.9(1), N1−Pd−C12 95.6(1), N2−Pd−C12 174.9(1).

As far as we know, in the case of species having N,N chelating ligands, complex **4** is the first one arising from ethene insertion into a palladium−acyl bond to be characterized in the solid state.

In conclusion we have shown that with an unsymmetric 6-substituted-2,2′-bipyridine, at least in the presence of the noncoordinating Brookhart's anion, bis-chelated complexes such as **4** are selectively formed and are stable even in the solid state. For comparison, it must be underlined that, although acetyl migration to ethene occurs also in the case of the analogous complex with the unsubstituted 2,2′-bipyridine, the correspond-

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(10) Irradiation, in the ^{1}H NMR spectrum of **3**, of the resonance at δ 1.57 (s, Pd-CH$_3$) results in enhancement of the doublet at δ 8.62 (H6′ bipy-6-Me).

(11) Selected ^{1}H−^{1}H NOESYcorrelations: δ 2.44 (Pd-CH$_2$) with δ 8.12 (bipy H6′) and δ 2.75 (CH$_2$CO); δ 2.75 with 2.44 and 2.36 (MeCO); δ 2.71 (bipy-6-Me) with δ 7.40 (bipy H5).

(12) In the ^{1}H NMR spectra a second set of signals of low intensity (ca. 10%) is likely to be due to a palladium enolate[3d] (^{1}H NMR, CDCl$_3$, δ 1.21 Me, d, 6.4 Hz; δ 4.32, CH, q, 6.4 Hz; 2.32 s MeCO, 2.76 s bipy-6-Me).

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ing bis-chelated complex could not be isolated, being unstable even at low temperature.[2g] Thus it seems that in the case of 2,2′-bipy the 6-substituent has an influence on the stabilization of species such as **4** which are relevant to alkenes/CO copolymerization. Their role is very complicated: they can affect the chain propagation in a number of ways.

At present it is not easy to find a rationale for the peculiar stability of complex **4**. Even the X-ray data, which give evidence, inter alia, for a rather long Pd−N(2) distance—elongation likely essential to relieve the steric effects of the substituent—do not allow a clear-cut conclusion owing to the lack of data for molecules having comparable N,N and C−O rings bound to palladium.

The influence of the nature of the 6-substituent on the stability of species such as **1**−**4** is hardly predictable. As we have recently reported, the behavior of these ligands (R alkyl, benzyl, aryl), particularly in palladium chemistry, is rather erratic.[13]

Experimental Section

All solvents were purified by standard techniques. [Pd(Me)-Cl(COD)][14] (COD = *Z*,*Z*-1,5-cyclooctadiene), 6-methyl-2,2′-bipyridine (HL),[15] and Na[BAr′$_4$][16] were synthesized via the published routes. IR spectra were recorded using a Perkin-Elmer spectrophotometer 983. NMR spectra were recorded with a Varian VXR300 spectrometer, operating at 299.9 MHz for ^{1}H and at 75 MHz for ^{13}C. Chemical shifts, in ppm, are relative to TMS for ^{1}H and ^{13}C. The mass spectrum was obtained with a VG 7070EQ instrument operating under FAB conditions with 3-nitrobenzyl alcohol as a supporting matrix. Elemental analyses (C, H, N) were performed by Mr. Antonello Canu in the Microanalytical Laboratory of our Department.

Synthesis of [Pd(Me)Cl(HL)] (1). To a solution of HL (386 mg, 2.27 mmol) in 20 mL of diethyl ether was added (under stirring at 20 °C) [Pd(Me)Cl(COD)] (541 mg, 2.04 mmol) dissolved in 10 mL of benzene. A pale yellow precipitate formed immediately, and the suspension was stirred for 2 h. The product was filtered off, washed with diethyl ether, and dried in vacuo, yielding 641 mg of the analytical sample. Yield = 96%, mp 173−174 °C. Anal. Calcd for $C_{12}H_{13}ClN_2Pd$: C, 44.05; H, 3.98; N, 8.56. Found: C, 43.79; H, 4.02; N, 8.39. Selected IR and NMR data: IR (Nujol, ν_{max}/cm^{-1}) 1595 m, 1562 m; ^{1}H NMR (CDCl$_3$) δ 1.28 (s, 3H, Me-Pd), 3.07 (s, 3H, bipy-6-Me), 7.32−8.07 (6H, aromatics), 8.62 (d, 1H, H6′). MS-FAB: *m*/*z* (%): 311(15) [M − Me]$^+$, 291(42) [M − Cl]$^+$, 276 (100) [M − Me − Cl]$^+$.

Synthesis of [Pd(MeCO)Cl(HL)] (2). A yellow solution of **1** (402 mg, 1.23 mmol) in 10 mL of dichloromethane was placed in a 100 mL flask connected to a vacuum line. The flask was evacuated and subsequently filled with carbon monoxide to a pressure of 1 bar. This sequence was repeated twice, and then the mixture was stirred 10 min, at 20 °C, until the solution became yellow-green. The flask was opened, the solution filtered through Celite, and the filter washed with dichloromethane (2 × 5 mL). The combined filtrates were evaporated to small volume, and diethyl ether was added. A yellow precipitate was filtered off and washed with diethyl ether (2 × 5 mL) to obtain 398 mg of the analytical sample.

Yield = 91%; mp 134−136 °C. Anal. Calcd for $C_{13}H_{13}ClN_2OPd$: C, 44.14; H, 3.68; N, 7.92. Found: C, 43.89; H, 3.59; N, 7.71. Selected IR and NMR data: IR (Nujol, ν_{max}/cm^{-1}) 1687 m, 1594 m, 1562 m; (CH$_2$Cl$_2$,ν_{max}/cm^{-1}) 1697 s, 1597 m; ^{1}H NMR (CDCl$_3$) δ 2.94 (br, 3H, bipy-6-Me), 2.69 (s, 3H, MeC-(O)-Pd), 7.30−8.09 (6H, aromatics), 8.42 (br, 1H, H6′). MS-FAB: *m*/*z* (%) 319 (30) [M − Cl]$^+$, 291(35) [M − CO − Cl]$^+$, 276 (100) [M − C(O)Me − Cl]$^+$.

Synthesis of [Pd{CH$_2$CH$_2$C(O)Me}(HL)][BAr′$_4$] (4). To a solution of **2** (379 mg, 1.06 mmol) in dichloromethane (50 mL), under stirring, at room temperature, were added 946 mg of Na[BAr′$_4$] (1.06 mmol). The color of the solution fades, and instantaneously a precipitate of NaCl is formed. The reaction vessel was satured with ethene for 10 min. The solution was filtered on Celite, then evaporated to dryness. The solid residue was washed with pentane and filtered to obtain the analytical sample as a pale orange solid. Yield: 81%; mp 103−5 °C. Anal. Calcd for $C_{47}H_{29}BF_{24}N_2OPd$: C, 46.61; H, 2.40; N, 2.31. Found: C, 46.25; H, 2.34; N, 2.46. Selected IR and NMR data: IR (Nujol, ν_{max}/cm^{-1}) 1622 m; 1606 w, 1277 s; 1125 br; (CH$_2$Cl$_2$,ν_{max}/cm^{-1}), 1615 s; 1566 m; ^{1}H NMR (CDCl$_3$) δ 2.36 (s, 3H, COMe), 2.44 (t, 2H, Pd-CH$_2$), 2.71 (s, 3H, bipy-6-Me), 2.75 (t, 2H, Pd-CH$_2$-C*H*$_2$), 7.34−7.95 (18H, aromatics), 8.12 (d, 1H, H6′); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 24.38 (MeCO); 25.04 (*C*H$_2$-Pd); 27.77 (Me-bipy); 49.54 (*C*H$_2$-CH$_2$-Pd); 119.42, 123.24, 126.64, 128.38, 139.70, 140.10 (aromatic C-H bipy); 149.98 (C6′ bipy); 152.12, 157.60, 161.54 (aromatic C bipy); 238.95 (CO-Pd); 117.49 (C$_{para}$ [BAr′$_4$]$^-$ $^3J_{C-F}$ = 4.0 Hz); 124.98 (CF$_3$ [BAr′$_4$]$^-$ $^1J_{C-F}$ = 272.6 Hz); 128.98 (C$_{meta}$ [BAr′$_4$]$^-$ $^2J_{C-F}$ = 31.4 Hz, $^3J_{C-B}$ = 2.8 Hz); 134.76 (C$_{ortho}$ [BAr′$_4$]$^-$ broad); 161.71 (C$_{ipso}$ [BAr′$_4$]$^-$ $^1J_{C-B}$ = 50.0 Hz). An APT experiment allowed us to distinguish between the methyl and methylene groups. MS-FAB: *m*/*z* (%): 347 (100) [M]$^+$, 291(ca. 20) [M − CH$_2$ − CH$_2$CO]$^+$, 276(96) [M − CH$_2$ − CH$_2$ − CO − Me]$^+$.

X-ray Structure Determination. Crystal data for **4**: $C_{47}H_{29}BF_{24}N_2OPd$, $M = 1210.94$, triclinic space group $P\bar{1}$ (no. 2), $a = 12.810(1)$ Å, $b = 12.969(2)$ Å, $c = 16.842(2)$ Å, $\alpha = 108.84(1)°$, $\beta = 101.58(1)°$, $\gamma = 105.54(1)°$, $U = 2421.4(6)$ Å^3, $Z = 2$, $D_c = 1.661$ g cm^{-3}, $\mu = 5.0$ cm^{-1}, $F(000) = 1200$, $T = 200$ K; reflections measured 29 323, independent 11 295 with $R_{int} = 0.021$. Empirical absorption correction, SADABS[17] ($T_{max} = 1.00$, $T_{min} = 0.92$). Final R_2 (F^2, all reflections) = 0.074, R_{2w} = 0.113, conventional $R_1 = 0.044$ for 778 parameters; Bruker SMART CCD area-detector, Mo Kα radiation ($\lambda = 0.71073$ Å), ω scan mode, $\theta_{min} = 3°$, $\theta_{max} = 26°$. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms with the exception of three fluorine atoms having occupancy factors of 0.20, which were refined isotropically. Many fluorine atoms are disordered, as often found for the same anion.[18] The six methylic hydrogen atoms were located in the final Fourier maps and not refined; the remaining hydrogen atoms were placed in calculated positions and also not refined. The program used was Personal SDP[19] on a Pentium III PC.

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Supporting Information Available: X-ray structure information for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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