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Preliminary communication

Alkene insertion reactions of nitrogen-coordinated acylpalladium(II) complexes. The crystal structure of the dicyclopentadiene insertion product $[Pd(C_{10}H_{12}COMe)(bpy)]SO_3CF_3$

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Abstract

The new acylpalladium(II) complex [PdI(COMe)(bpy)] (**2b**, bpy = 2,2′-bipyridyl) has been obtained by two routes; (i) by insertion of carbon monoxide into the Pd–C bond of [PdIMe(bpy)] (**1b**), and (ii) by ligand exchange from [PdI(COMe)(tmeda)] (**2a**, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethanediamine). The cationic species obtained by reaction of **2a** and **2b** with $AgOSO_2CF_3$ both undergo alkene insertions into the Pd–C acyl bond that lead to remarkably stable products. The X-ray structure of the dicyclopentadiene insertion product $[Pd(C_{10}H_{12}COMe)(bpy)]SO_3CF_3$ (**4b**) shows the oxygen atom of the carbonyl group to be coordinated to the metal center (Pd–O = 2.026(3) Å).

Recent developments in organometallic palladium chemistry have provided some novel complexes with N-donor ligands that have properties in metal-mediated organic synthesis and catalysis complementary to those of the widely used phosphine complexes. For instance [Pd(H(CN)C=CHCN)(bpy)] is used as a catalyst for the cross-coupling of β-hydrogen-containing alkyl halides with Me_4Sn, a process that has not been observed with phosphine complexes [1]. Our interest in nitrogen-coordinated palladium(II) complexes is concerned not only with their properties in cross-coupling reactions but also their reactivity in respect of insertion of alkenes into the palladium–carbon bond. Some recent examples of insertion of alkenes into the Pd–C bond of arylpalladium complexes were reported by Chiusoli et al. and Cheng et al. [2]. Acylpalladium complexes appear to be more susceptible towards alkene insertion [3], but up to now the studies have been

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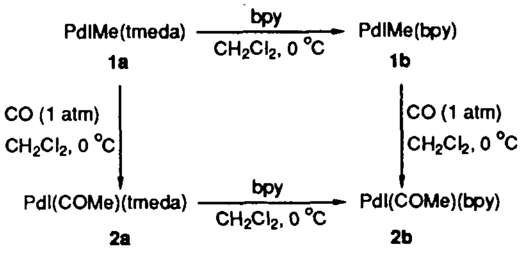
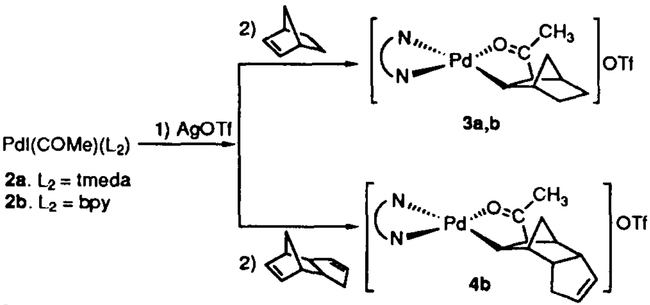


Scheme 1.

restricted to phosphine complexes, such as $PdX(COMe)(PPh_3)_2$ (X = Cl, Br or I) and $[Pd(COR)(MeCN)(PPh_3)_2]BF_4$ (R = Me or Ph) [3a], which contain an acyl group stable towards de-insertion of carbon monoxide.

Recently, both neutral [4–6] and cationic [7,8] mono-organopalladium(II) complexes bearing nitrogen-donor ligands have been reported to react with CO to afford stable acylpalladium(II) compounds. For example, PdXMe(tmeda) (X = Cl, Br, I) reacts cleanly and in high yield with CO to afford the acyl complexes PdX(COMe)(tmeda) [5]. We now report the initial results of a study of the reactivity of nitrogen-coordinated acylpalladium(II) complexes towards alkene insertion using PdI(COMe)(tmeda) (**2a**) and the new complex PdI(COMe)(bpy) (**2b**).

Compound **2b** can be prepared in high yield via two routes (Scheme 1), *viz.* (i) by ligand exchange from PdI(COMe)(tmeda) (**2a**) [5,9*] or (ii) by insertion of CO into the Pd–C bond of PdIMe(bpy) (**1b**) [10*,12*]. The complexes **2a** and **2b** do not react with alkenes, indicating either that insertion through a five-coordinate intermediate (i.e. by an associative process) is not possible or that reaction via a dissociative route (e.g. prior iodine or ligand dissociation) is blocked. The latter possibility is supported by the observation that treatment of **2a** and **2b** with silver trifluoromethanesulphonate ($AgOSO_2CF_3$) followed by reaction with an alkene (Scheme 2) does lead to alkene insertion products [13*–15*,17*]. Surprisingly, Sen et al. found that the analogous bis-phosphine complex $PdI(COMe)(PPh_3)_2$ does react smoothly with alkenes to the insertion products within a few hours [3a].



Scheme 2.

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* Reference number with asterisk indicates a note in the list of references.

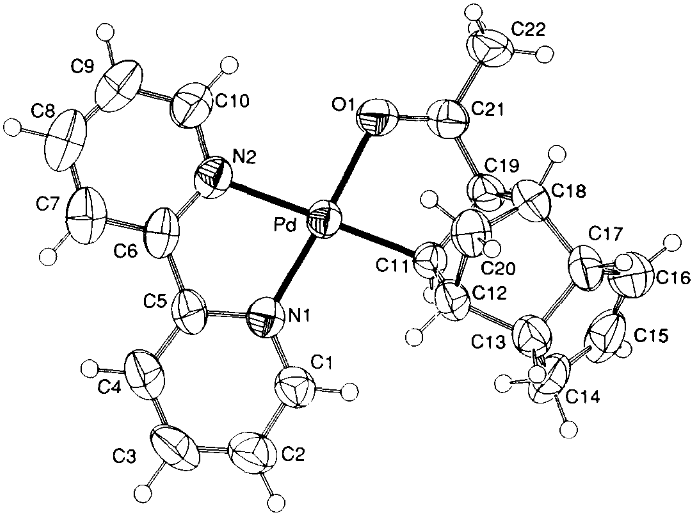

Fig. 1. Thermal motion ellipsoid plot (50% probability level) for one isomer of the cation $[Pd(C_{10}H_{12}COMe)(bpy)]^+$ [18*].

The alkene insertion products **3a,b** and **4b** are remarkably stable and can be handled in air at room temperature for at least several hours. Crystals of the dicyclopentadiene insertion product $[Pd(C_{10}H_{12}COMe)(bpy)]SO_3CF_3$ (**4b**) suitable for an X-ray structural study [19*] were obtained from CH_2Cl_2/Et_2O. The molecular structure of **4b** (see Fig. 1) shows the carbonyl group to be coordinated to the metal (Pd–O = 2.026(3) Å) to form a five-membered PdCCCO chelate ring. The palladium center in **4b** has a square planar environment comprising the 2,2′-bipyridyl ligand, which occupies two adjacent positions (the Pd–N1 and Pd–N2 bond lengths are 2.013(3) and 2.121(4) Å, respectively; N1–Pd–N2 = 79.50(15)°), and the C,O chelate bonded ligand. The Pd–C11 distance for the latter ligand (2.023(4) Å) is comparable with those found for other sp^3 carbons *trans* to a sp^2 nitrogen atom (2.036(6) Å) [6,20]. The C21–O1 bond length (1.249(6) Å) is typical for a carbonyl group [21*] and is comparable with the C–O bond length in the bis-phosphine compound (1.240(10) Å) [3a]. The X-ray structure clearly shows that the dicyclopentadiene [16*] moiety has reacted selectively, in an *exo* mode, with the 5,6 rather than the 2,3 double bond [18*]. This structural feature could not be identified from the NMR spectra. The *exo* mode of insertion is consistent with the results of Sen et al., who were able to show that insertion of norbornylene in $[Pd(COMe)(MeCN)(PPh_3)_2]BF_4$ also takes place on the *exo* face of the norbornylene moiety [3a].

The single carbonyl stretching vibration frequency (ν(C–O)) found for **3a,b** and **4b** has in all cases a rather low value, *viz.* 1595 cm^{-1} (**3a**), 1598 cm^{-1} (**3b**) and 1601 cm^{-1} (**4b**). These values are a consequence of the coordination of the carbonyl group to the palladium center (*cf.* the bis-phosphine complex $[Pd(C_7H_{10}COMe)(PPh_3)_2]BF_4$ which has a ν(C–O) of 1620 cm^{-1} [3a]). The analogous platinum(II) compound $[Pt(C_7H_{10}COMe)(PPh_3)_2]BF_4$ has a ν(C–O) value of 1595 cm^{-1} (very similar to those for **3a,b** and **4b**) that was attributed to a lowered C–O bond order for the carbonyl group [22]. However, this is not reflected in the C–O bond length of this bis-phosphine compound (1.240(10) Å [3a]) or of **4b** (1.249(6) Å) reported here. We thus believe that the carbonyl stretching frequency in these complexes is merely lowered by coordination to the metal and that the low ν(C–O) value need not necessarily be associated with a lowered bond order. The higher ν(C–O) value for the bis-phosphine complex indicates that the carbonyl group is more weakly bound to the palladium in this compound than in the bis-amine complexes. This can also be seen from the Pd–O bond distance, which is significantly longer for the bis-phosphine compound (2.114(6) Å [3a]) than for **4b** (2.026(3) Å).

The availability of nitrogen-coordinated acyl-palladium complexes has made possible comparative studies of the influence of phosphine and nitrogen donor ligands on the reactivity of acyl-palladium complexes. From the above results the reactivities of the cationic species towards alkenes are found to be closely comparable. The neutral compounds, however, show a major difference in reactivity, since the nitrogen coordinated compounds do not undergo insertion of alkenes whereas the phosphine compounds do. At present it is unclear whether this difference should be attributed to the difference in donor strength between nitrogen and phosphorus or whether the chelate effect of the bidentate nitrogen donor ligands is the main factor.

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9 **2b**: to a solution of 0.16 g (0.41 mmol) of PdI(COMe)(tmeda) (**2a**) in 50 mL of CH$_2$Cl$_2$ was added, at 0°C under nitrogen, 0.20 g (1.28 mmol) of 2,2′-bipyridyl. After 16 h stirring the volatiles were evaporated *in vacuo* and the residue washed with diethyl ether (3 × 50 ml) and dried *in vacuo*. Yield 0.15 g (85%). M.p. 181°C (dec). Anal. Found: C, 33.32; H, 2.57; N, 6.48. C$_{12}$H$_{11}$IN$_2$OPd calc.: C, 33.19; H, 2.56; N, 6.35%. ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si (ext)): δ 2.71 (s, 3H, COCH_3); 7.43 (m, 1H, bpy); 7.49 (m, 1H, bpy); 7.98 (m, 1H, bpy); 8.11 (m, 2H, bpy); 8.25 (m, 2H, bpy); 9.16 (d, 1H, bpy). ^{13}C NMR (75 MHz, CDCl$_3$, Me$_4$Si (ext)): δ 42.98 (CH$_3$); 121.84, 122.69, 126.28, 126.63, 138.96, 139.18, 150.13, 151.72, 152.27, 154.47 (bpy); 205.69 (CO). IR (KBr): ν(C–O) = 1678 cm^{-1}.

10 The synthesis of PdIMe(bpy) (**1b**) was carried out by the procedure used for **2b** starting from PdIMe(tmeda) [9*]. Yield 97%. ^{1}H NMR data were consistent with those reported by Canty et al. [11], who prepared **1b** by oxidative addition of MeI to Pd$_2$(dba)$_3$ (dba = dibenzylideneacetone) in the presence of bpy in 79% yield.

11 P.K. Byers and A.J. Canty, Organometallics, 9 (1990) 210.

12 An ice-cooled solution of 1.13 g (2.8 mmol) of PdIMe(bpy) (**1b**) in 100 mL of CH$_2$Cl$_2$, under nitrogen, was treated with CO (1 atm) for 1 min, after which the vessel was closed. Stirring was continued for 2.5 h and the solution then filtered through filter aid and the volatiles evaporated *in vacuo* to give pure **2b**. Yield 1.17 g (97%).

13 A typical procedure for the insertion of alkenes was as follows: To an ice-cooled solution of 0.20 g (0.46 mmol) of PdI(COMe)(bpy) (**2b**) in 50 mL of CH_2Cl_2 were added 2.0 mL of MeCN, 56.4 mg (0.60 mmol) of norbornylene, and 0.16 g (0.62 mmol) AgOTf. A white solid immediately separated. After 3 h stirring at 0°C the solution was filtered through filter aid and the volatiles evaporated *in vacuo*. The greenish-white residue was washed once with 80 mL of Et_2O to remove residual MeCN and dried *in vacuo*. Yield 0.23 g (91%).

14 Physical data for the alkene-insertion products:
3a: Yield 93%. M.p. 89°C (dec.). Anal. Found: C, 37.76; H, 5.75; N, 5.50. $C_{16}H_{29}F_3N_2O_4SPd$ calc.: C, 37.13, H, 5.21; N, 5.58%. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si (ext)): δ 1.30 (m, 4H, norb.); 1.61 (m, 2H, norb.); 2.07 (m, 2H, norb.); 2.27 (s, 3H, CH_3); 2.41 (d, 1H, norb.); 2.57 (s, 3H, NMe_2); 2.62 (s, 3H, NMe_2); 2.65 (m, 4H, norb. or tmeda); 2.66 (s, 3H, NMe_2); 2.71 (s, 3H, NMe_2); 2.97 (m, 1H, norb. or tmeda). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si (ext)): δ. 27.20 (CH_3); 29.35, 29.51, 36.62 (CH_2, norb.); 41.54, 42.94 (CH, norb.); 47.63 (NMe_2); 48.15 (CH, norb.); 48.52, 50.49, 52.61 (NMe_2); 56.61, 63.96 (CH_2, tmeda); 70.93 (CH, norb); 196.61 (CO). IR (KBr): ν(C–O) = 1595 cm^{-1}.
3b: Yield 91%. M.p. 115°C (dec.). Anal. Found: C, 43.77; H, 3.86; N, 5.10. $C_{20}H_{21}F_3N_2O_4SPd$ calc.: C, 43.49; H, 3.97; N, 5.19%. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si (ext)): δ 1.36 (d, 1H, norb.); 1.47 (m, 2H, norb.); 1.74 (m, 2H, norb.); 1.90 (d, 1H, norb.); 2.26 (d, 1H, norb.); 2.48 (s, 3H, $COCH_3$); 2.57 (d, 1H, norb.); 2.69 (d, 1H, norb.); 2.91 (d, 1H, norb.); 7.64 (m, 2H, bpy); 8.21 (m, 2H, bpy); 8.34 (d, 1H, bpy); 8.56 (m, 3H, bpy). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si (ext)): δ 27.51, 29.66, 29.75, 36.96, 43.04, 43.34, 52.76, 70.83 (norb. and CH_3); 123.63, 124.67, 127.29, 127.67, 140.72, 140.98, 148.52, 150.40, 152.23, 156.62 (bpy); 187.86 (CO). IR (KBr): ν(C–O) = 1598 cm^{-1}.
4b: Yield 85%. M.p. 141°C (dec.). Anal. Found: C, 47.07; H, 3.95; N, 4.77. $C_{23}H_{23}F_3N_2O_4SPd$ calc.: C, 46.31; H, 3.89; N, 4.67%. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si (ext)): δ 1.65 (6H, alkyl and H_2O); 2.1–3.3 (12H, alkyl); 5.6–5.9 (mmm, 2H, alkenyl, isomer ratio ca. 1:1.7); 7.64 (m, 2H, bpy); 8.24 (m, 3H, bpy); 8.62 (m, 3H, bpy). ^{13}C NMR (50 MHz, CD_2Cl_2, Me_4Si (ext)): δ 27.46, 27.61, 32.86, 33.33, 39.59, 40.13, 42.63, 43.19, 44.76, 46.23, 47.21, 47.64, 48.36, 49.42, 65,42, 67.96, 123.33, 124.39, 127.84, 128.03, 131.36, 132.15, 132.37, 133.40, 140.91, 141.11, 149.14, 150.64, 150.81, 152.62, 157.23 (alkyl, alkenyl and bpy), 185.21, 186.44 (CO). IR (KBr): ν(C–O) = 1601 cm^{-1}.

15 Complex **3a** reacted with dicyclopentadiene [13*] to give the insertion product, as shown by the alkene-signals (300 MHz, $CDCl_3$) of the 2,3 double bond [16*] at 5.38, 5.54, 5.61 and 5.70 ppm (isomer ratio ca. 1:1) and the ν(C–O) of 1599 cm^{-1}. The insertion product was not obtained in pure form.

16 The systematic name for dicyclopentadiene is 3a,4,7,7a-tetrahydro-4,7-methanoindene.

17 Owing to the presence of two isomers in commercial dicyclopentadiene, which differ only in the position of the peripheral double bond, we also obtained two isomers for **4b**, as shown by NMR spectroscopy [14*] and X-ray diffraction [18*].

18 The fact that the observed bond distances for C14–C15 and C15–C16 differ only slightly, with values in between those for a single and double bond, suggests that these bond distances are the average for two isomeric forms. Only one form is shown here (see Fig. 1).

19 Crystal data for **4b**: $C_{23}H_{23}F_3N_2O_4SPd$, space group $P2_1/n$; cell dimensions a 8.3086(4), b 15.3894(6), c 18.1479(9) Å, $\beta = 99.98(1)°$; $Z = 4$; $V = 2285.36(19)$ Å^3; $d_{calc} = 1.7057(1)$ g·cm^{-3}. A room temperature dataset was obtained with an Enraf–Nonius CAD4T diffractometer [Rotating anode; Mo-K_α (graphite monochromator); $\lambda = 0.71073$ Å; $\theta_{max} = 27.5°$] for a crystal [0.12 × 0.23 × 0.60 mm] sealed in a Lindemann glass cappillary. The structure was solved using 3136 reflections (corrected for absorption [DIFABS]) with $I > 2.5\sigma(I)$ [SHELXS86/PATT]. Full matrix refinement with SHELX76 converged at $R = 0.042$ [$R_w = 0.034$; $w^{-1} = \sigma^2(F)$]. Hydrogen atoms were introduced on calculated positions. A table of atomic coordinates and a complete list of bond lengths and bond angles has been deposited with the Cambridge Crystallographic Data Center.

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21 A search in the datafiles of the Cambridge Crystallographic Data Center revealed a mean C–O bond length of 1.255(28) Å for eight comparable ketones coordinated via the oxygen atom to a transition metal.

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