

Isolation of Alkyl- and Acyl-palladium Complexes containing Rigid Bidentate Nitrogen Ligands by Stepwise Successive Insertion of CO and Alkenes†

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Fast successive stoichiometric insertions of carbon monoxide and norbornadiene ($R'CH=CHR''$) have been observed into Pd–C bonds of neutral $[Pd(Me)Cl(An-bian)]$ leading to thermally stable multiinsertion products of the type $Pd-C(O)-CH(R')-CH(R'')-C(O)-Me$ **4** and $Pd-CH(R')-CH(R'')-C(O)-CH(R')-CH(R'')-C(O)-Me$ **5**, the stability of which is due to the rigidity of the bidentate nitrogen ligands employed; these are the first isolated and fully characterized compounds which are models for intermediates in the copolymerization of carbon monoxide and alkenes.

Studies of the mechanism of copolymerization reactions of CO and alkenes (ethene) currently receive increasing attention.^{1–4} Evidence has been obtained for sequences of perfectly alternating insertions of CO and alkenes into Pd–C bonds, but also a mechanism involving Pd–carbene intermediates has been put forward.⁵ So far, no compounds of the type $[L_nPd\{CH(R')-CH(R'')-C(O)-\}_n-R]$ have been isolated and/or treated stoichiometrically with the complementary monomer. We describe here the synthesis and isolation of relevant oligomeric alkyl- and acyl-palladium compounds, which have been fully characterized and which subsequently can be treated stepwise with CO or norbornadiene, respectively, to give new isolable complexes.

The employment of new palladium compounds containing the rigid bidentate nitrogen ligand Ar-bian† as a catalyst in homogeneous catalytic C–C bond formation⁶ and hydrogenation⁷ reactions has provided us with the insight that the bian ligand not only has an enhancing effect on reactivity of low-valent Pd complexes, but is also more suitable than all bidentate nitrogen ligands reported thus far to stabilize Pd^{IV} in e.g., triorgano- Pd^{IV} compounds, and Pt^{IV} even in cationic triorgano- Pt^{IV} complexes.⁸ We reasoned that by using Ar-bian as the ancillary ligand, intermediates in the copolymerization of alkenes and CO which so far have been elusive might be stabilized and isolated.‡

Reaction of $[Pd(Me)Cl(An-bian)]$ **1**, prepared from $[Pd(Me)Cl(cod)]$,⁹ and An-bian, with CO (1 bar) at 20 °C in dichloromethane afforded, after 5 min stirring and subsequent isolation by filtration and evaporation of the solvent, 81% of

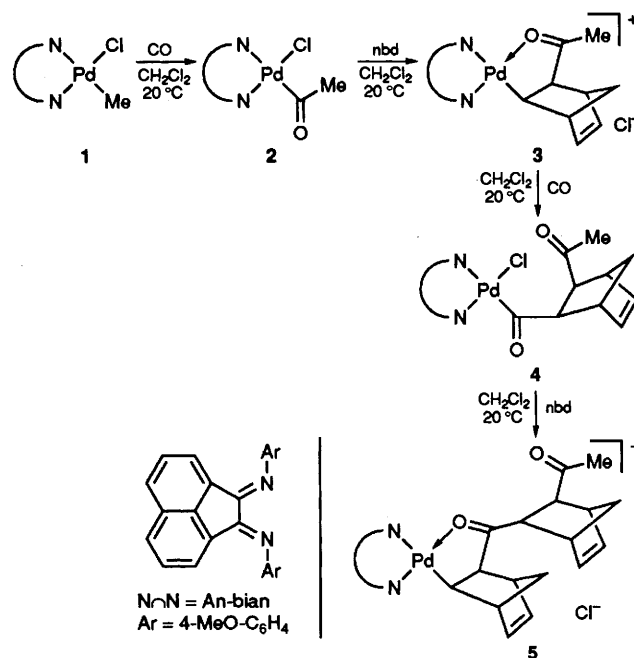
† bian = bis-iminoacenaphthene; in general Ar-bian stands for the bis(arylimino) derivatives. In the study described here, An-bian was employed (An = 4-MeOC₆H₄).

‡ *In situ* studies have provided spectroscopic evidence for possible intermediates, see e.g. refs. 3, 4, 10.

red-brown $[\text{Pd}\{\text{C}(\text{O})\text{Me}\}\text{Cl}(\text{An-bian})]$ **2** (Scheme 1).[§] Addition of 1.05 equiv. of norbornadiene (nbd) to a solution of **2** in dichloromethane at 20 °C and 30 min stirring at that temperature resulted in 91% of dark red $[\text{Pd}\{\text{C}_7\text{H}_8\text{-C}(\text{O})\text{Me}\}\text{Cl}(\text{An-bian})]\text{Cl}$ **3**.[§] When **3** was treated with CO as above for the reaction of **1**, a brown solid was obtained in 80% yield, which analysed correctly for and was spectroscopically authenticated as $[\text{Pd}\{\text{C}(\text{O})\text{-C}_7\text{H}_8\text{-C}(\text{O})\text{Me}\}\text{Cl}(\text{An-bian})]$ **4**.[§] Subsequent treatment of a solution of **4** as described for **2** gave an 87% isolated yield of the new alkylpalladium complex $[\text{Pd}\{\text{C}_7\text{H}_8\text{-C}(\text{O})\text{-C}_7\text{H}_8\text{-C}(\text{O})\text{Me}\}(\text{An-bian})]\text{Cl}$ **5**,[§] which was spectroscopically fully identified. Elemental analysis was carried out on the trifluoromethanesulfonate derivative **5a**. The presence of two different carbonyl units was confirmed by carrying out the reactions of **1** and **3** with ^{13}CO .

This sequence of synthesis and isolation of each compound, followed by subsequent conversion by a stoichiometric reaction to the next oligomeric stage unequivocally demonstrates the feasibility of these successive insertions in palladium-catalysed copolymerization. In fact, we have obtained a *living oligomeric system* which can be enlarged at will. Further insertions of CO and nbd into **5** occur readily, but complete assignment by NMR spectroscopy is hampered by the similarity of subsequent alkene and CO units after the stage of **5**.

In the alkyl complexes **3** and **5** the oxygen atom of the carbonyl group is coordinated to the Pd-centre, as was inferred from conductivity data, \uparrow a strong IR band at *ca.* 1600



Scheme 1

[§] Complex **2** (from chloroform-hexane), Found: C, 57.7; H, 4.2; N, 4.9. $\text{C}_{28}\text{H}_{23}\text{ClN}_2\text{O}_3\text{Pd}$ requires C, 58.25; H, 4.0; N, 4.9%. $^1\text{H NMR}$ δ (CDCl_3): 8.04, 7.47, 6.8 (br) (naphthene); 7.27, 7.03, 3.88 (an); 2.23 [$\text{Pd-C}(\text{O})\text{Me}$]; $^{13}\text{C NMR}$ δ (CDCl_3): 131.7, 131.5, 129.0, 126.8, 125.4 (naphthene); 159.6, 144.5, 123.1, 115.2, 56.1 (an); 223.4 [$\text{PdC}(\text{O})\text{Me}$]; 33.8 [$\text{PdC}(\text{O})\text{Me}$]; IR ν/cm^{-1} (KBr): 1709 (C=O), 1615 (C=N), 315 (Pd-Cl).

Complex **3**, $^1\text{H NMR}$ δ (CDCl_3): 8.14, 7.54, 7.18 (naphthene); 7.38, 7.13, 3.94 (An); 2.00 (dd, J 6.2, 1.9 Hz, Pd-CH), 2.47 [d, J 6.2 Hz, $\text{CH-C}(\text{O})\text{Me}$]; 3.00, 2.38 (2 bridgehead), 1.66 (d), 1.28 (d, J 9.0 Hz, CH_2), 5.96 (dd, J 5.2, 2.8 Hz), 5.48 (dd, J 5.2, 3.0 Hz, 2=CH); 2.53 [$\text{Pd-C}(\text{O})\text{Me}$]; $^{13}\text{C NMR}$ δ (CDCl_3): 170.1, 146.0, 132.7, 131.8, 129.2, 126.0, 125.7 (naphthene); 160.2, 138.8, 123.9, 115.5, 56.3 (An); 50.0 (Pd-C), 62.9 [$\text{C-C}(\text{O})\text{Me}$], 48.8, 47.0 (2 CH), 45.9 (CH_2), 135.6, 134.2 (2=CH); 236.0 [$\text{PdC}(\text{O})\text{Me}$]; 28.8 [$\text{PdC}(\text{O})\text{Me}$]; IR ν/cm^{-1} (KBr): 1602 (C=O \rightarrow Pd).

Complex **4**, Found: C, 61.8; H, 4.6; N, 4.15. $\text{C}_{36}\text{H}_{31}\text{ClN}_2\text{O}_4\text{Pd}$ requires C, 62.0; H, 4.5; N, 4.0%. $^1\text{H NMR}$ δ (CDCl_3): 8.04, 7.46; 7.1 (naphthene); 7.3 (br), 3.87 (An); 4.04 [d, J 8.9 Hz, Pd-C(O)-CH], 2.10 [$\text{CH-C}(\text{O})\text{Me}$]; 3.00, 2.86 (2 bridgehead), 0.79 (d), 0.66 (d, J 9.0 Hz, CH_2), 6.13 (dd, J 5.5, 3.0 Hz), 6.05 (dd, J 5.5, 3.0 Hz, 2=H); 2.10 [$\text{Pd-C}(\text{O})\text{Me}$]; $^{13}\text{C NMR}$ δ (CDCl_3): 171.2, 144.7, 131.8, 131.7, 129.0, 127.1, 125.8 (naphthene); 159.6, 124.0, 115.2, 56.1 (An); 55.0, 44.7, 43.6 (3 CH), 139.1, 137.2 (2=CH); 222.0 [$\text{Pd-C}(\text{O})$], 210.1 [$\text{C}(\text{O})\text{-Me}$], 31.8 [$\text{PdC}(\text{O})\text{Me}$]; IR ν/cm^{-1} (KBr): 1699 (br, C=O), 317 (Pd-Cl).

Complex **5**, Found for **5a**: C, 58.3; H, 4.3; N, 3.0. (Calc. for $\text{C}_{44}\text{H}_{39}\text{F}_3\text{N}_2\text{O}_7\text{PdS}$ requires C, 58.5; H, 4.35; N, 3.1%. $^1\text{H NMR}$ δ (CDCl_3): 8.11, 7.49, 7.18 (naphthene); 7.31 (br), 3.88 (An); 1.84 (dd, J 5.8, 1.7 Hz, Pd-CH), 2.38 [d, J 5.8 Hz Pd-CH-CH-C(O)]; 3.05, 2.20 (2 bridgehead), 1.39 (d), 1.18 (d, J 9.2 Hz, CH_2), 5.95 (dd, J 5.3, 2.9 Hz), 5.40 (dd, J 5.3, 3.1 Hz, 2=CH) for norbornyl bonded to Pd; 3.33, 2.09, 3.05, 2.48, 1.41, 6.28 (dd), 6.03 (dd) for norbornyl between CO moieties; 2.09 [$\text{C}(\text{O})\text{Me}$]. $^{13}\text{C NMR}$ δ (CDCl_3 , 233 K): 175.6, 144.7, 133.0, 131.7, 129.3, 126.3, 126.2 (naphthene); 160.5, 123.6, 115.8, 56.5 (An); 50.8, 50.2, 50.0, 49.6, 47.7, 46.9 (2 \times 3 CH), 63.8, 62.7 [2 CH-C(O)], 138.7, 138.6, 135.1, 134.7 (4=CH); 241.2 [$\text{C}(\text{O})\text{-Me}$], 208.7 [$\text{CH-C}(\text{O})\text{-CH}$]; 29.7 [$\text{C}(\text{O})\text{Me}$]; IR ν/cm^{-1} (KBr): 1703 (C=O), 1598 (C=O \rightarrow Pd).

\uparrow Partly coincident with $\nu(\text{C}=\text{C})$ of bian, but the increased intensity after insertion [and labelling with ^{13}CO which leads to $\nu(\text{CO})$ at *ca.* 1550 cm^{-1}] leave no doubt that this band is mainly due to $\nu(\text{CO})$ of an *O*-coordinated organic carbonyl. Compound **3** [derivative with *N*-(*o,o'*- $\text{Pr}_2\text{-C}_6\text{H}_3$)] exhibits a high equivalent conductance of 80.9 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ compared to **1** and **2** (3.3 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$), in agreement with dissociated Cl for **3** (and by analogy also **5**) and coordinated Cl for **1**, **2** and **4** (the latter by analogy).

cm^{-1} , \uparrow the ^{13}C resonance at δ 240 for Pd-C₇H₈-C(O)-R, and, for **3**, the Pd-C₇H₈-C(O)-Me ^1H resonance at δ 2.5. Insertion of CO after alkene insertion has been observed before as a secondary reaction after reaction of norbornene with $[\text{Pd}\{\text{C}(\text{O})\text{Me}\}\text{Cl}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}]$,¹⁰ but the acyl complex **4** as well as the products of further reaction of **4** with nbd, *i.e.* **5** and **5a**, constitute the first examples of both isolated and fully characterized compounds of this kind. The enhanced stability of the present acyl palladium complexes with respect to deinsertion of CO has also been observed for rigid tridentate ligands;¹¹ these are stable at 20 °C, whereas complexes containing more flexible ligands, *e.g.* diphosphines¹⁰ or 2,6-(Me₂NCH₂)₂-pyridine,¹² are readily decarbonylated.

Insertion of norbornadiene invariably took place at the *exo*-face, as was concluded from the observed $^3J(\text{H}_{13}\text{-H}_{19})$ of 5.6–6.7 Hz¹³ and no evidence for the formation of nortricyclenyl derivatives was found. Norbornene and dicyclopentadiene insert more sluggishly than nbd and mixtures were obtained in these cases, whereas for simple alkenes mainly starting materials were observed.

Interestingly, the neutral compounds **2** and **4** are very reactive in the alkene insertion, which must be accounted for by dissociation of Cl⁻ in order to accommodate the alkene in a *cis*-position within the coordination plane. Apparently, the rigidity of the bidentate nitrogen ligand plays an important role by shutting off of competing processes, which take place in the case of other ancillary ligands. In the case of non-rigid bidentate P- and N-ligands, two effects are operative: (i) the angle P-M-P or N-M-N can within limits be adjusted to accommodate insertion (hence also a deinsertion pathway is available) and (ii) dissociation of one of the donor atoms of the chelating ancillary ligand is favoured (next to dissociation of Cl) owing to the strong *trans*-influence and *trans*-effect of the alkyl (or acyl) group. In the case of bian, these processes are not possible. So, although only a small amount of Cl-dissociated complex may be present for **2** and **4**, because of the small *trans*-influence of N as compared to P (which is corroborated by their very low equivalent conductance), there will be, apart from five-coordinate routes, no other pathways available. Furthermore, β -elimination from **3** or **5** is not a viable process and deinsertion is slow. These should take place through dissociation of the *O*-coordinated carbonyl moiety, which will be more pronounced for P- than for N-ligands. Decarbonylation from **2** and **4** will also be slower for the

N-ligands, as Cl *trans* to N will be more sluggishly displaced than from similar diphosphine complexes.

In conclusion, it has been shown that the An-bian ligand activates a Pd-alkyl complex for alternating insertion of CO and nbd and stabilizes the products by virtue of their donor character and rigidity. The isolation of 2-5 as (models for) living cooligomers and their stepwise further reaction with CO and nbd provide evidence for a mechanism of copolymerization *via* alternating insertions of CO into the palladium-alkyl and of alkene into the palladium-acyl bond.

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