

more readily abstracted than methyl hydrogens,^{14a} and the rate differences are especially large in 1,5-hydrogen transfer reactions of sp² carbon-centred radicals.^{14b} For substrate **4a**, the favourable geometry provided by the amide linker is not sufficient to overcome the lack of reactivity of a methyl hydrogen.

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Anion-controlled Oligomerization of Carbon Monoxide and Norbornene on a Palladium(II) Centre

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The insertion of both norbornene and carbon monoxide into the Pd–C bond of 2,2'-bipyridyl coordinated palladium(II) complexes can be controlled by the nature of the anions present in solution, and this allows the stepwise synthesis of a metal-bound CO/norbornene co-oligomer of which an X-ray crystal structure is presented.

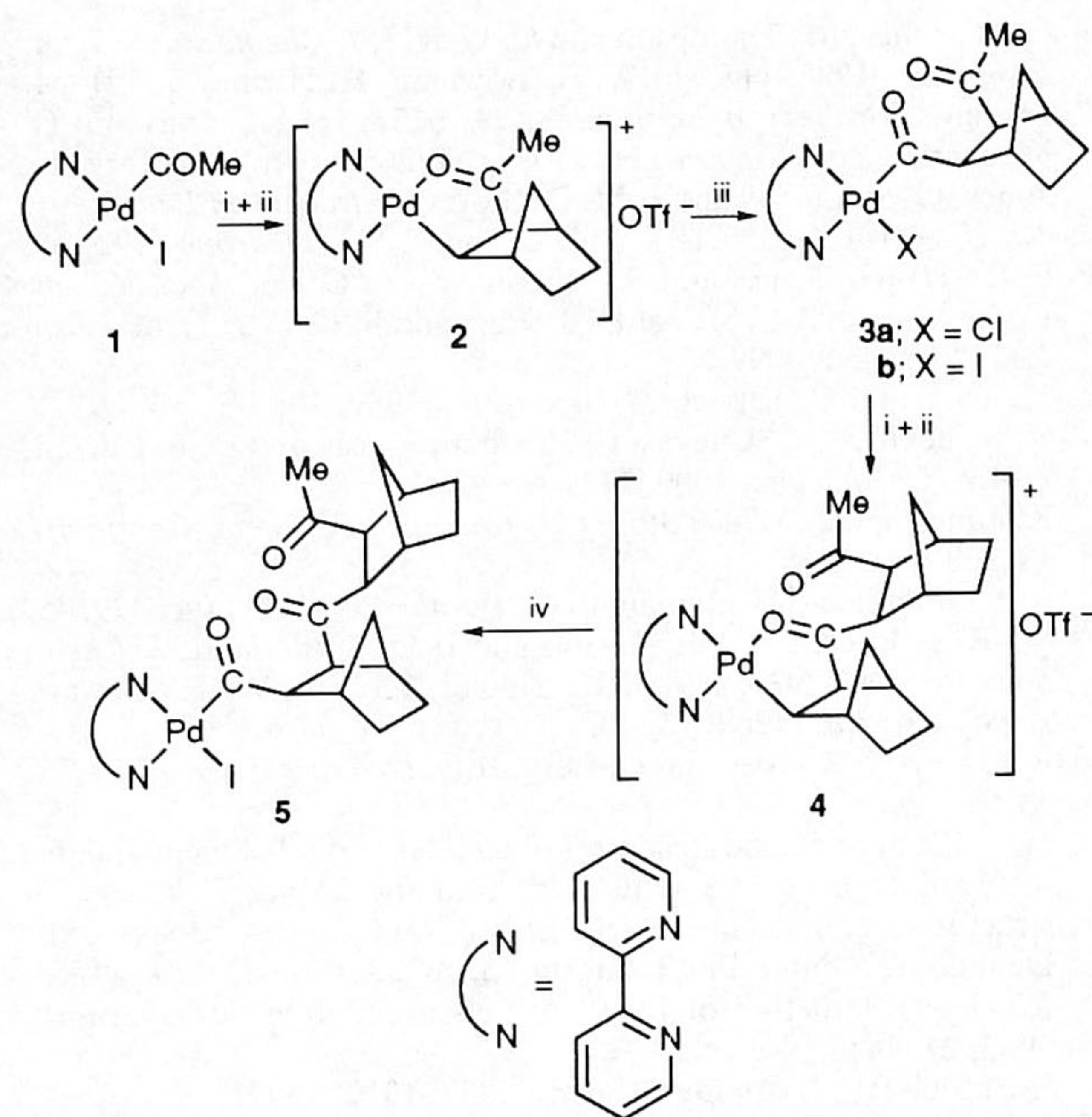
Extensive studies of the migratory insertion of unsaturated molecules into metal–carbon bonds have given rise to useful applications, among which the synthesis of alternating copolymers of carbon monoxide and alkenes has been realised.^{1,2} The copolymerization of carbon monoxide and ethylene, using palladium(II) complexes as homogeneous catalysts, has been especially well studied in the past few years.^{1,2} Several parameters that can influence these reactions have been evaluated and recently, Drent *et al.* have shown that the correct choice of both the ligands and the anions is crucial in these catalysed copolymerization reactions.² So far, however, methods that allow the controlled, stepwise build-up of the CO/alkene polymer chain have not been reported.

We now report a new approach to the stepwise construction of a CO/alkene copolymer with complete control of the intermediate steps: the sequential insertion of CO and norbornene into the Pd–C bond of complexes containing the bidentate nitrogen-donor ligand 2,2'-bipyridyl (bpy) and the important influence exerted by the anions in the reaction mixture is described. These studies include the first X-ray

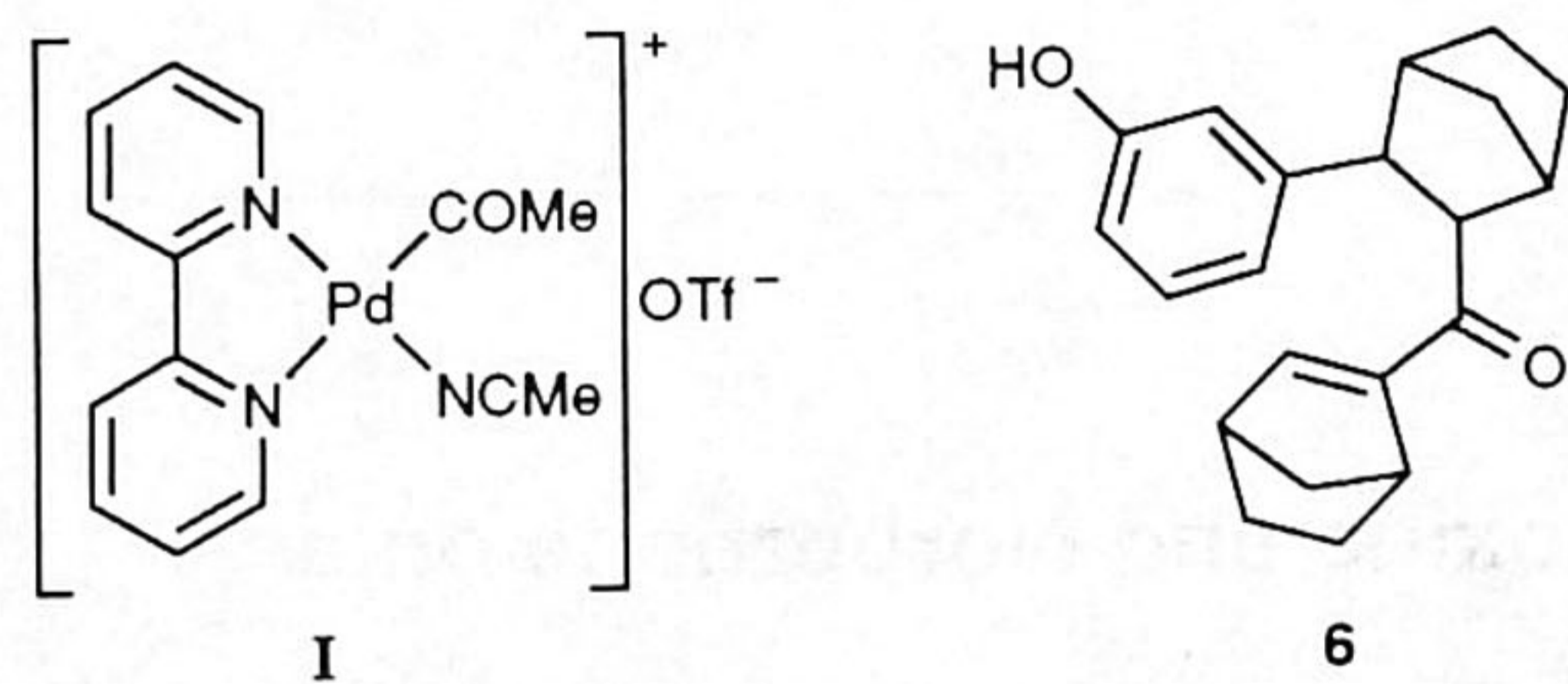
crystal structure of a metal-bound oligomer of norbornene and CO.

Recently, we published results of the synthesis of acetyl-palladium(II) complexes containing bidentate nitrogen-donor ligands, *e.g.* bpy.³ The complex PdI(COMe)(bpy) (**1**, Scheme 1) can be converted to the ionic intermediate [Pd(COMe)(MeCN)(bpy)]OTf (**I**, OTf = trifluoromethanesulfonate), which is able to insert strained alkenes to afford alkyl complexes such as [Pd(C₇H₁₀COMe)(bpy)]OTf (**2**, C₇H₁₀ = *cis*, *exo*-norbornyl).³ This first step in our sequence of the modelling of the copolymerization process is now followed by the second step—the insertion of CO into the palladium–alkyl bond of **2**. Although initial attempts to directly insert carbon monoxide into the Pd–C bond of **2** did not give an isolable acyl complex, we have now discovered that addition of a large excess of a sodium halide,† *i.e.* a more than 20 equiv.

† Similar observations were obtained *in situ* by Vrieze *et al.* for a phosphorus-coordinated palladium complex.¹³



Scheme 1 Reagents and conditions: i, AgOTf, 0 °C, MeCN + CH₂Cl₂; ii, norbornene, 0 °C, CH₂Cl₂; iii, CO (1 atm.), NaX, -30 °C, acetone; iv, CO (1 atm.), NaI, -30 °C, acetone



excess of NaCl or NaI, prior to CO addition affords isolable, neutral, CO-inserted acyl complexes **3a** (83%) and **3b** (93%) in 18 and 6 h, respectively (Scheme 1).[‡]

Having found the correct conditions for both insertion of norbornene into acyl complex **1** (to afford alkyl complex **2**) and for the further reaction of **2** with carbon monoxide in the presence of halide anions to give the double insertion products **3a,b**, the next step is to attempt another insertion of norbornene (the second in our sequence). In a logical extension we find that the insertion of norbornene can be successfully accomplished, analogously to the synthesis of **2**, by treating either **3a** or **3b** first with silver trifluoromethanesulfonate (AgOTf) and then with norbornene (Scheme 1). This affords complex **4** which was obtained in 98% yield.[‡] Our novel ionic alkyl complex **4**, which contains two carbonyl and two substituted norbornyl fragments, shows a characteristic low frequency IR stretching vibration at 1582 cm⁻¹ for the carbonyl group coordinating to the metal (*cf.* **2**, 1598 cm⁻¹).³ The IR absorption of the other carbonyl group is at 1708 cm⁻¹, which is normal for an organic ketone functionality. The ¹³C NMR resonances[‡] of the carbonyl carbon atoms of **4** have characteristic positions, *i.e.* at δ 243.4 for the one coordinated *via* its oxygen atom to the metal (*cf.* 240.8 for **2**)³ and at δ 208.0 for the other.

[‡] Selected spectroscopic data for **3a**: ¹³C NMR, (CDCl₃) δ (rel. to SiMe₄) 210.9, 230.6 (CO); IR (KBr), ν/cm⁻¹ 1710, 1672. **3b**: ¹³C NMR, δ 211.4, 229.7 (CO); IR, 1706, 1663. **4**: ¹³C NMR, 208.0, 243.4 (CO); IR, 1708, 1582. **5**: ¹³C NMR, δ 210.8, 213.3, 232.7 (CO); IR, 1715, 1669.

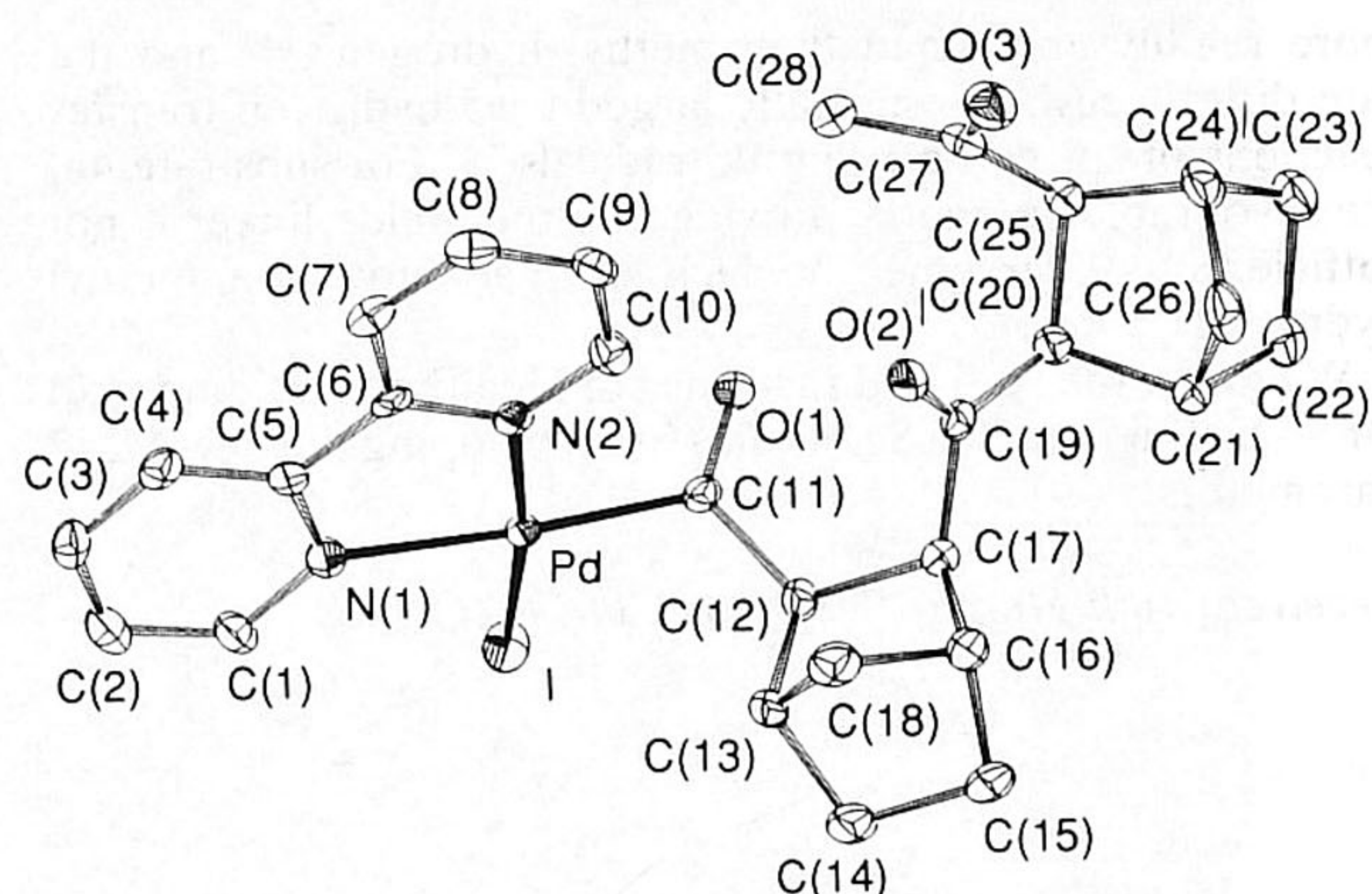


Fig. 1 ORTEP drawing (50% probability level) of **5**§ with the adopted numbering scheme. Hydrogen atoms and the acetone solvent molecule are omitted for clarity. Selected bond distances (Å), bond angles (°) and torsion angles (°): Pd-N(1) 2.161(4), Pd-N(2) 2.098(4), Pd-C(11) 1.952(5), Pd-I 2.5912(7), N(1)-Pd-N(2) 77.8(2), C(11)-Pd-I 86.9(2), Pd-C(11)-O(1) 121.3(4), I-Pd-N(1)-C(5) 161.4(3), I-Pd-N(1)-C(1)-10.5(5).

Starting from compound **4**, in the presence of sodium iodide (20 equiv.), we have now accomplished a further successful insertion of carbon monoxide (the second in our sequence) into a palladium-C(alkyl) bond and hereby arrive at the new, isolable acyl complex **5** (Scheme 1) in 88% yield.[‡] This neutral complex, which is the result of the stepwise anion-controlled sequential insertion reactions of norbornene, CO, norbornene and CO starting from acetyl complex **1**, is no less than a metal-bound cooligomer of CO and norbornene. It has been recrystallized from neat acetone to give crystals suitable for an X-ray structural analysis (Fig. 1).[§]

The asymmetric unit of the crystal structure contains one molecule of **5** together with one acetone solvent molecule. In the molecular structure of **5**, the metal centre has a slightly distorted square-planar surrounding which consists of a bidentate *N*-bonded bpy ligand [N(1), N(2)], an iodide anion [I(1)] and a *C*-bonded acyl group [C(11)-O(1)]. The total molecular structure of the organic substituent of the acyl group is fully consistent with our spectroscopic analysis of this

[§] Crystal data for **5**: C₂₈H₃₁IN₂O₃Pd·C₃H₆O, *M_r* = 734.97, yellow, plate-shaped crystal (0.4 × 0.4 × 0.05 mm), triclinic, space group *P*1̄ (No. 2) with *a* = 10.128(2), *b* = 11.655(2), *c* = 13.633(2) Å, α = 109.89(1), β = 100.58(1), γ = 92.92(2)°, *V* = 1476.3(4) Å³, *Z* = 2, ρ_c = 1.653 g cm⁻³, *F*(000) = 736, μ(Mo-Kα) = 16.9 cm⁻¹, 8978 reflections measured, 6770 independent (1.63° < θ < 27.50°, ω/2θ scan, Δω = 0.81 + 0.35 tan θ°, *T* = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD4 Turbo diffractometer with a rotating anode. Data were corrected for Lorentz polarisation and for a linear decay of 5% of the reference reflections (2̄ 2 4, 2̄ 2 4̄, 4̄ 3 2) during 26 h of X-ray exposure time; empirical absorption correction applied (DIFABS, correction range 0.777–1.209). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92). Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76); final *R* value 0.044, *wR* = 0.057, *w* = 1/[σ²(*F*) + 0.001107*F*²], *S* = 2.05, for 354 parameters and 5061 reflections with *I* > 2.5σ(*I*). Hydrogen atoms were included in the refinement on calculated positions (C-H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with an overall isotropic thermal parameter of 0.041(3) Å². Weights were introduced in the final refinement cycles. A final difference Fourier showed no residual density outside -1.32 and 1.34 e Å⁻³ (near Pd or I). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

compound, *i.e.* there is no interaction of the three carbonyl groups present with the metal or with each other. Around the metal centre, besides the expected angular deviations resulting from the five-membered chelate ring [$\text{N}(1)\text{-Pd-N}(2) = 77.8(2)^\circ$] the most noticeable distortion is concerned with the position of the iodide that lies $0.32(2) \text{ \AA}$ above the coordination plane defined by Pd, N(1), N(2) and C(11) on the same side as the C(11)-O(1) keto function. The Pd-I [$2.5912(7) \text{ \AA}$] and the Pd-C(11) (acyl) bond distances [$1.952(2) \text{ \AA}$] have values expected for these bonds *trans* to a pyridine nitrogen.^{4,5} Concerning the CO/norbornene oligomer moiety, the carbonyl carbon atom [C(11)] connected to the palladium centre shows true sp^2 character and the C(12)-C(11)-O(1) plane is oriented almost perpendicular to the metal coordination plane [$89.8(2)^\circ$]. Both norbornene moieties are found *cis*, *exo* substituted as expected^{3,6} and are *syn* positioned with respect to each other. This latter positioning indicates that the orientation of the second norbornene before and during insertion is governed by the first inserted norbornene. This is consistent with reports on the stereospecific character of the copolymerization of CO with norbornene⁷ and other alkenes,⁸⁻¹¹ and confirmed by the X-ray structure of compound **6** with *syn* geometry isolated from a palladium-catalysed norbornene-carbon monoxide cooligomerization reaction by Chiusoli *et al.*¹²

Our results show that by variation of the anion of palladium(II) complexes it is possible to trap intermediates arising during the copolymerization of CO and norbornene so that a stepwise study of this process is now possible. Moreover, our procedure seems well suited for the rational synthesis of selectively substituted CO/alkene polymers towards which our current research is directed.

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Complete Reversal of Stereoselectivity in Rhodium Complex-catalysed Hydrosilylation of Alk-1-yne

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[Rh(cod)Cl]₂-catalysed hydrosilylation of hex-1-yne with Et₃SiH in EtOH or DMF is highly selective for the formation of (*Z*)-vinylsilane, whereas [Rh(cod)Cl]₂-PPh₃ in MeCN or PrⁿCN is highly selective for the formation of (*E*)-vinylsilane; the active species for *cis* addition has been revealed to be Rh^I cationic complex generated *in situ*.†

Hydrosilylation of alkynes has synthetic value, because the vinylsilane products are versatile intermediates in organic synthesis.¹ The most straightforward and simple method for the preparation of vinylsilanes is hydrosilylation of alkynes. With alk-1-yne, the formation of three isomers is possible, and much effort has been expended in developing highly selective hydrosilylation.²

In the course of our studies,³ we investigated Rh-catalysed hydrosilylation of hex-1-yne with Et₃SiH in various solvents; both stereoisomers were obtained in high yields with high selectivities by choosing the reaction conditions.

The hydrosilylation of hex-1-yne with Et₃SiH was carried out in various solvents, using [Rh(cod)Cl]₂ as a catalyst [eqn. (1)]. Results are summarized in Table 1. A high degree of selectivity forming (*Z*)-vinylsilane **1** was attained using EtOH or DMF (entries 5 and 6). The reactions in benzene, acetone

Table 1 [Rh(cod)Cl]₂-catalysed hydrosilylation of hex-1-yne with Et₃SiH^a

Entry	Solvent	Yield (%) ^b	Product ratio ^c		
			1	2	3
1	Benzene	85	82	15	3
2	Acetone	89	68	29	3
3	THF	68	90	5	5
4	CH ₂ Cl ₂	91	77	13	10
5	EtOH	85	94	4	2
6	DMF	80	97	1	2
7 ^{d,e}	MeCM	93	2	97	1
8 ^d	MeCN	18	36	33	31
9 ^{d,e}	Pr ⁿ CN	85	2	96	2

^a A mixture of hex-1-yne (8 mmol), Et₃SiH (12 mmol), [Rh(cod)Cl]₂ (0.004 mmol) and solvent (12 ml) was stirred at room temp. for 41 h. ^b Isolated yield based on the amount of hex-1-yne charged. ^c Determined by ¹H NMR. ^d [Rh(cod)Cl]₂ (0.012 mmol). ^e PPh₃ (0.048 mmol).

† Abbreviations used: cod = cycloocta-1,5-diene, DMF = dimethylformamide, THF = tetrahydrofuran.