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Comments on the catalytic alkoxycarbonylation of alkynes

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The alkoxycarbonyl complexes $Pd(Ph_2Ppy)_2(CO_2R)(OAc)$ where Ph_2Ppy is 2-pyridyldiphenylphosphine and R = Me **1**, Et **2**, i-Pr **3** have been prepared from $Pd(OAc)_2$ and Ph_2Ppy in ethanol solution under an atmosphere of CO. Increasing the CO pressure favours the formation of palladium carbonyl species. In the presence of 2 mol equivalents of CF_3CO_2H, the complex $Pd(Ph_2Ppy)_2(CO_2CH_3)(CF_3CO_2)$ **4** is isolated from methanol. $Pd(Ph_2Ppy)_2(CO_2CH_3)Cl$ **5** has been obtained by the reaction of $Pd(Ph_2Ppy)_2Cl_2$ with $NaOCH_3$ in the presence of CO. **1** and **5** have been crystallographicaly characterised as *trans* isomers, a geometry confirmed for all the complexes by ^{13}C NMR. The reactivity of the complexes toward alkynes and propadiene has been investigated and the π-allyl complex $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3)=CH_2\}][O_2CCF_3]$ **8** isolated and structurally characterised.

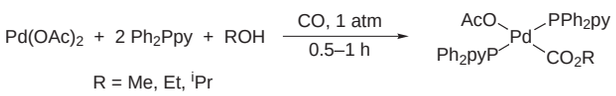
Introduction

Transition metal alkoxycarbonyl complexes are potential intermediates in a number of catalytic carbonylation reactions. Examples include the hydrocarboxyalkylation of alkenes and alkynes to esters, the cyclocarbonylation of ethynyl alcohols to lactones and CO–alkene copolymerisation.[1] In processes where the formation of a metal–alkoxycarbonyl intermediate is invoked, the observed product, *e.g.* carboxylic ester, results from the insertion of an unsaturated hydrocarbon into a pre-formed M–C(O)OR bond with subsequent protonolysis to the ester. An alternative mechanism proceeds by hydrometallation of the alkene (Pd–H precursor) followed by carbonylation and alcoholysis. Evidence exists for both these cycles and the operation of one or other or both is likely to depend on the specific reaction and reaction conditions.

Complexes generated *in situ* from mixtures of palladium acetate, 2-pyridyldiphenylphosphine and sulfonic acids are spectacular catalysts for the methoxycarbonylation of propyne to methylmethacrylate (MMA) both in terms of their high activity and superior selectivity under mild conditions.[2] With this in mind we have undertaken a study on the coordination and reaction chemistry of this catalyst system. One or other of the catalytic mechanisms alluded to above, namely the hydride and methoxycarbonyl cycles, may be in operation during catalysis. Drent and co-workers have presented a compelling argument for the operation of the latter based on selectivity improvements obtained on increasing the steric bulk of the phosphine.[3] More recently others have provided equally cogent evidence for the existence of a hydride mechanism.[4] We have recently presented observations on the behaviour of palladium complexes of 2-pyridyldiphenylphosphine with weakly coordinating oxo-anions.[5] In this paper we present a series of new alkoxycarbonyl complexes of the type $Pd(Ph_2Ppy)_2(CO_2R)X$ which are relevant to the general study of Drent type catalysis. The nature of these new species is examined with emphasis on their reactivity toward terminal alkynes and allene (a known poison in these reactions).

Results and discussion

The alkoxycarbonyl complexes **1**–**3** are obtained from a solution of $Pd(OAc)_2$ and Ph_2Ppy in the appropriate alcohol under ambient pressure carbon monoxide (Scheme 1). They



Scheme 1

are poorly soluble in the medium of their preparation and precipitate as white, air-stable crystalline solids in moderate yield. The dimer $Pd_2(Ph_2Ppy)_2(OAc)_2$ was detected in the mother liquor after isolating **1**–**3** and its formation is largely responsible for the modest yields of the alkoxycarbonyl complexes.

In the presence of 2 mol equivalents of trifluoroacetic acid, $Pd(Ph_2Ppy)_2(CO_2CH_3)(O_2CCF_3)$, **4**, is obtained from the 1:2 mixture of $Pd(OAc)_2$:Ph_2Ppy in methanol. As expected, when the proportion of acid is increased, the complex $Pd(Ph_2Ppy)_2(CF_3CO_2)_2$ is formed by substitution of the alkoxycarbonyl ligand. An attempt to extend the range of acids to include sulfonic acids failed, the reactions affording mixtures of uncharacterised products. Irrespective of the pressure of CO employed, the preparation of $Pd(Ph_2Ppy)_2(CO_2CH_3)Cl$, **5**, from $Pd(Ph_2Ppy)_2Cl_2$ requires the presence of sodium methoxide to prevent quantitative formation of the unwanted Pd(I) dimer $[Pd_2(Ph_2Ppy)_2Cl_2]$. Complex **5** was also obtained by treatment of the cationic complex $[Pd(Ph_2Ppy)_2Cl][OTf]$, which contains a bidentate Ph_2Ppy ligand, with sodium methoxide and carbon monoxide. Attempts to isolate a Ph_2Ppy chelate complex with a bound pyridyl nitrogen from **5** by chloride abstraction with silver salts ($AgBF_4$ or AgOTf) were unsuccessful, the starting complex being decomposed to uncharacterised products. The $^{31}P\{^1H\}$ NMR spectrum of the recovered solid was free of resonances due to a cationic palladium species.

For all the complexes, the best yields were obtained under carbon monoxide at atmospheric pressure. When the carbon monoxide pressure was increased, mixtures containing carbonyl complexes were formed as identified by the characteristic ν(CO) bands at *ca.* 1830 cm^{-1} in the infrared spectra. The carbonylation reactions with higher alcohols are more susceptible to formation of carbonyl complexes at the higher limits of carbon monoxide pressure. Formation of stable palladium carbonyl complexes, under similar carbonylation conditions and in the presence of trialkylamines, has been reported to give the complexes $Pd(CO)(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_3$.[1f]

Table 1 Selected spectroscopic data for the Ph_2Ppy complexes

Complex	$^{31}P\{^1H\}$ [a] NMR	Infrared $\nu(CO_2R)/cm^{-1}$	Infrared $\nu(OAc)/cm^{-1}$
1 $Pd(Ph_2Ppy)_2(CO_2Me)(OAc)$ [b]	16.26	1659.4s, 1071.9 (br)	1603.1vs
2 $Pd(Ph_2Ppy)_2(CO_2Et)(OAc)$ [d]	21.4	1658.9s, 1099.5/1059.0s	1612.6s
3 $Pd(Ph_2PPy)_2(CO_2i\text{-}Pr)(OAc)$ [d]	18.5	1653.1s, 1099.5/1051.3s	1610.7s
4 $Pd(Ph_2Ppy)_2(CO_2CH_3)(CF_3CO_2)$ [b]	15.40	1687.5vs	
5 $Pd(Ph_2Ppy)_2(CO_2Me)Cl$ [c]	18.52	1679.7vs, 1096.9/1059.0vs	
6 $Pd(Ph_2Ppy)_2(C{\equiv}CPh)(CF_3CO_2)$ [c]	22.2	2098s	
7 $Pd(Ph_2Ppy)_2(C{\equiv}CCH_3)(CF_3CO_2)$ [c]	21.9	2104s	

[a] δ in ppm. [b] In C_6D_6. [c] In $CDCl_3$. [d] In CD_3CN.

Table 2 ^{1} NMR data (δ) of the alkoxycarbonyl complexes

	H(6)	H(7)	H(8)	H(9)	Other ligands
1 [a]	6.53dd	8.60dt	—	8.42d	8.2–8.35 (m, 4H), 7.0–7.3 (m, 7H), 2.63 (s, CO_2Me), 1.50 (v, br, OAc)
2 [c]	6.62dd	8.49dt	—	8.76d	8.15–8.3 (m, 4H), 7.0–7.3 (m, 7H), 3.23 (q, 7.12), 0.51 (t, 7.19), 1.47 (s, OAc)
3 [c]	6.59dd	8.44dt	—	8.81d	8.3 (m, 4H), 7.1 (m, 6H), 4.32 (spt, 6.3, 1H), 0.46 (d, 6H), 1.43 (br, OAc)
4 [a]	6.58dd		—	8.47d	8.1–8.3 (m, 5H), 7.1–7.3 (m, 7H), 2.53 (CO_2Me)
5 [b]	7.27dd	8.23dt	7.68t	8.74d	7.9 (m, 4H), 7.4 (m, 6H), 2.38 (s, CO_2Me)

[a] In C_6D_6. [b] In $CDCl_3$. [c] In CD_3CN.

Initial formation of the divalent complex $Pd(Ph_2Ppy)_2(OAc)_2$ is presumed to occur during the synthesis of **1**–**3**, with subsequent displacement of one of the acetate ligands by the alkoxycarbonyl group. In the absence of carbon monoxide, dimeric $Pd_2(Ph_2Ppy)_2(OAc)_2$ is the only isolable product from the 1:1 reaction of $Pd(OAc)_2$ and Ph_2Ppy. We have previously observed $Pd(Ph_2Ppy)_2(OAc)_2$ as a transient species in the preparation of $Pd_2(Ph_2Ppy)_2(OAc)_2$.[5] The ^{31}P NMR spectrum of a 1:2 mixture of $Pd(OAc)_2$ and Ph_2Ppy in C_6D_6/CH_3OH recorded shortly after dissolution has a major peak at δ 21.6. This is assigned to the redox unstable $Pd(Ph_2Ppy)_2(OAc)_2$. Introduction of carbon monoxide to this solution for a period of 30 minutes leads to the clean formation of $Pd(Ph_2Ppy)_2(CO_2CH_3)(OAc)$, **1** ($\delta$ 16.3), suggesting rapid formation of the desired product prior to any extensive decomposition of $Pd(Ph_2Ppy)_2(OAc)_2$ to the Pd(I)–Pd(I) dimer. The presence of the diacetate complex suggests that displacement of one of these ligands by methoxide prior to the introduction of CO is not occurring, and the alkoxycarbonyl complexes are the result of the attack of alcohol at a coordinated carbonyl after replacement of a bound acetate by CO. It seems reasonable to suggest that the more tightly bound chlorides in $Pd(Ph_2Ppy)_2Cl_2$ are less readily replaced by CO, hence the inability to isolate **5** by methods successful for **1**–**4**. The need for methoxide in the synthesis of **5** may suggest initial replacement of chloride by CH_3O^- and subsequent insertion of CO into the metal–alkoxide bond, *i.e.* an alternative mechanism to that purported for **1**–**4**. Unlike $Pd(Ph_2Ppy)_2(OAc)_2$, **1** is stable with respect to reductive dimerisation.

The complexes **1**–**5** give sharp singlets in their $^{31}P\{^1H\}$ NMR spectra with typical coordination shifts for phosphorus bound to monomeric Pd(II) (Table 1). In the ^{1}H NMR spectra, where assignable, the same pattern of resonances is observed as for the free Ph_2Ppy ligand (Table 2). In common with compounds of a similar type,[6] complexes **1**–**3** show the methoxy singlet at $\delta \approx 2.5$. The observation of virtual triplets for a number of pertinent carbon signals (notably C1, C2 and C5) in the ^{13}C NMR spectra indicates the *trans* geometry in all the complexes.[7] As expected for monodentate Ph_2Ppy, the ^{13}C chemical shifts for the complexes closely parallel those for the uncoordinated ligand (Table 3).

The IR spectra of **1**–**5** show very strong bands for the C=O and C–O stretches of the methoxycarbonyl groups in the region 1690–1650 cm^{-1} and 1100–1000 cm^{-1} respectively. These values compare well with those reported for similar complexes. The ν(C=O) of the acetate ligand appears in the region 1613–1603 cm^{-1}. The stretching frequency, ν(C=O), of the $CF_3CO_2^-$ ligand in complex **4** occurs at 1681 cm^{-1}, within the range expected for monodentate coordination (1680–1720 cm^{-1}).[8]

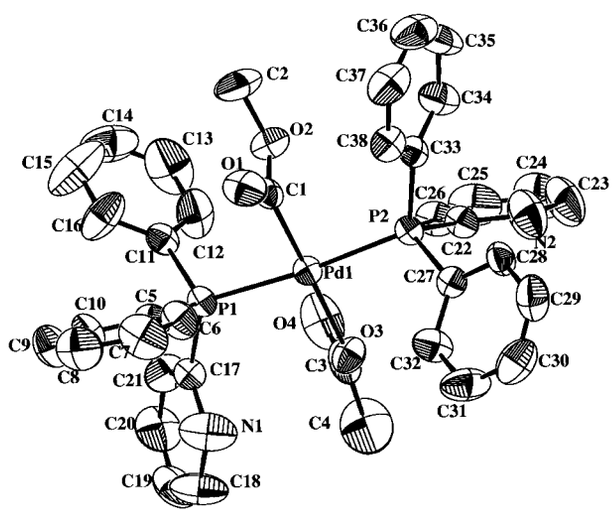


Fig. 1 Molecular structure of $Pd(Ph_2Ppy)_2(CO_2CH_3)(OAc)$ **1**.

Colourless crystals of **1** and **5** suitable for structural determination were obtained by slow diffusion of petroleum ether into a toluene solution of the appropriate complex. The molecular structures of compounds **1** and **5** with the adopted numbering scheme are shown in Figs. 1 and 2. Details of data collection and selected bond lengths and angles are summarised in Tables 4, 5 and 6. The coordination about the metal centre is square planar, with the phosphorus donors mutually *trans* as established in solution (see above). The acetate group in **1** acts as a unidentate ligand. Both the acetate and $^-CO_2CH_3$ ligand planes are perpendicular to the coordination plane. The Pd–C and Pd–O bond distances in **1** are 1.967(5) and 2.092(3) Å respectively, almost identical to the values of 1.984(4) and 2.116(3) Å for the PPh_3 analogue.[9] The Pd–P bond distances (av. 2.332(1) Å) are virtually identical with the PPh_3 complex

Table 3 $^{13}C\{^{1}H\}$ NMR data (δ) for the alkoxycarbonyl complexes[a]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	Other ligands
1	135.4 (t, 7)[b]	136.0 (t, 6)	131.7 (d, 3)	130.5 (s)	—	135.6 (s)	132.6 (d, 8.7)	124.0 (s)	150.1 (s)	180.1, 51.7 (s, CO_2CH_3); 30.4 (s, OAc)
2	—	134.5 (t)	127.6 (d)	130.1 (d)	—	135.3 (s)	131.3 (t)	123.8 (s)	149.4 (t)	60.5, 12.6 [s, $CH_3CH_2CO_2$], 22.5 (s, OAc)
3	—	134.83 (t, 6)	127.6 (t)	130.2 (s)	155.67 (t, 33)	135.2 (s)	131.34 (t, 13)	123.9 (s)	149.5 (t, 7)	174.69, 22.60 (s, OAc); 68.22, 20.69 {s, $(CH_3)_2CHCO_2$}
4	—	135.8 (t, 7)		130.9 (s)	—	—	131.2 (t, 14)	124.1 (s)	150.3 (s)	52.4 (s, CO_2CH_3)
5	131.3 (t, 24)	135.0 (t, 6)	128.1 (t, 4.6)	130.4 (s)	156.4 (t, 34)	135.6 (d, 3.6)	132.3 (t, 14.4)	124.1 (s)	150.0 (t, 7)	183.3, 51.96 (s, CO_2CH_3)
Ph_2PPy	136.2 (d, 12)	134.2 (d, 20)	128.7 (d, 7)	129.1 (s)	164.0 (d, 3)	135.8 (d, 2)	127.9 (d, 15)	122.2 (s)	150.4 (d, 13)	

[a] Complexes **1**, **2** measured in C_6D_6, **3** in $CDCl_3$, and **4**, **5** in CD_3CN. Assignments were made with the aid of DEPT measurements for all complexes except **3**. [b] Coupling constants are in Hz.

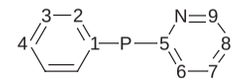


Table 4 Crystal data for $Pd(Ph_2Ppy)_2(CO_2Me)(OAc)$ **1**, $Pd(Ph_2Ppy)_2(CO_2Me)Cl$ **5** and $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3)=CH_2\}][O_2CCF_3]$ **8**

Compound	**1**	**5**	**8**
Empirical formula	$C_{38}H_{34}N_2O_4P_2Pd$	$C_{36}H_{31}ClN_2O_2P_2Pd$	$C_{42}H_{37}F_3N_2O_2P_2Pd$
Formula weight	751.01	727.42	827.08
T/K	150(2)	150(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2(1)/n$
a/Å	9.490(2)	18.084(9)	11.557(4)
b/Å	10.448(2)	15.609(8)	20.895(2)
c/Å	18.6230(13)	24.354(2)	15.5579(7)
α/°	74.544(9)		
β/°	79.718(6)	110.63(1)	92.767(10)
γ/°	80.364(9)		
V/Å^3	1737.1(5)	6434(5)	3753(2)
Z	2	8	4
D_{calc}/Mg m^{-3}	1.436	1.502	1.464
Absorption coefficient/mm^{-1}	0.669	0.795	0.634
F(000)	768	2960	1688
Crystal size/mm	0.11 × 0.11 × 0.24	0.29 × 0.18 × 0.11	0.36 × 0.11 × 0.25
θ/°	2.04 to 25.07	2.17 to 25.06	1.95 to 25.03
Index ranges	$-10 \le h \le 9$, $-12 \le k \le 10$, $-20 \le l \le 20$	$-21 \le h \le 20$, $-18 \le k \le 17$, $-27 \le l \le 19$	$-12 \le h \le 12$, $-23 \le k \le 23$, $-17 \le l \le 18$
Reflections collected	7266	12339	13837
Independent reflections	4747	4659	5355
R_{int}	0.0611	0.0547	0.0577
Data/restraints/parameters	4747/0/426	4659/6/398	5355/18/500
Goodness-of-fit on F^2	0.852	0.862	0.834
Final R indices	$R_1 = 0.0375$	$R_1 = 0.0400$	$R_1 = 0.0339$
$[I > 2\sigma(I)]$	$wR_2 = 0.0790$	$wR_2 = 0.0910$	$wR_2 = 0.0630$
R indices (all data)	$R_1 = 0.0525$, $wR_2 = 0.0813$	$R_1 = 0.0634$, $wR_2 = 0.0947$	$R_1 = 0.0533$, $wR_2 = 0.0651$
Largest diff. peak and hole/e Å^{-3}	0.552 and −0.437	0.939 and −0.451	0.609 and −0.300

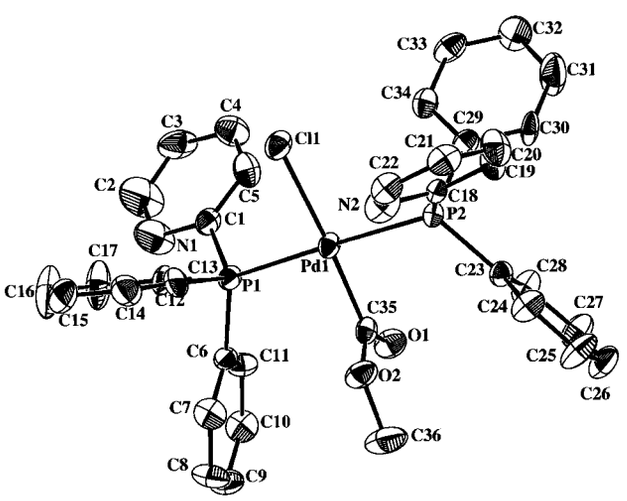


Fig. 2 Molecular structure of $Pd(Ph_2Ppy)_2(CO_2CH_3)Cl$ **5**.

(av. 2.339(1) Å). In like fashion, the Pd–C and Pd–Cl bond distances of 1.970(5) and 2.404(1) Å in the chloro-complex **5** are identical to those of the PPh_3 analogue. As in the acetate complex the $^-CO_2CH_3$ ligand is perpendicular to the coordination plane. The Ph_2Ppy groups in both complexes display a staggered conformation with respect to the P–Pd–P axis with no unusual intramolecular contacts observed for the pyridyl rings.

The average value of the Pd–C bond distance of the $PdL_2(CO_2CH_3)X$, (L = Ph_2Ppy, PPh_3, X = OAc, Cl^-) complexes is 1.974(5) Å, which accords with that expected from the sum of the covalent radii of carbon (sp^2) and palladium atoms (1.96 Å). Relatively short palladium–alkoxycarbonyl bonds have been reported.[9b] Apart from these crystallographic observations, low frequency infrared shifts have been seen for the ν(CO) bands in these complexes with respect to formate esters. This has led Bertani and co-workers to invoke a degree of double bond character in the Pd–C bond, resulting from electron back-donation from the palladium to the ligand, so that resonance structures involving Pd–C double bonds contribute to the stability of these compounds.[10] If such bonding does occur in the current complexes its contribution is believed to be small.

Table 5 Selected bond lengths (Å) and angles (°) for $Pd(Ph_2Ppy)_2(CH_3CO_2)(OAc)$

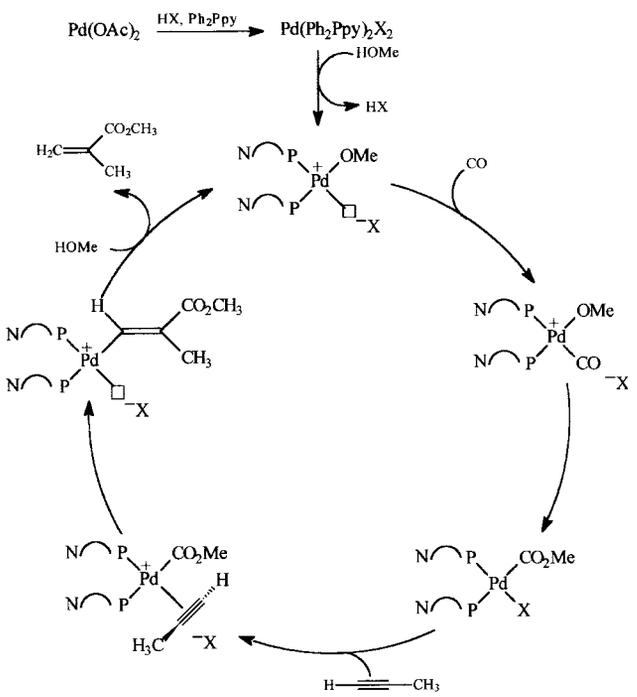
Pd(1)–C(1)	1.967(5)	Pd(1)–O(3)	2.092(3)
Pd(1)–P(2)	2.330(1)	Pd(1)–P(1)	2.333(1)
P(2)–C(33)	1.812(5)	P(2)–C(27)	1.817(5)
P(2)–C(22)	1.827(4)	P(1)–C(11)	1.809(5)
P(1)–C(17)	1.821(5)	P(1)–C(5)	1.822(4)
N(1)–C(17)	1.392(7)	N(1)–C(18)	1.422(7)
N(2)–C(22)	1.382(6)	N(2)–C(23)	1.392(7)
O(1)–C(1)	1.189(5)	O(2)–C(1)	1.353(6)
O(2)–C(2)	1.442(5)	O(3)–C(3)	1.283(6)
O(4)–C(3)	1.215(7)		
C(1)–Pd((1)–O(3)	176.8(2)	C(1)–Pd(1)–P(2)	88.9(1)
O(3)–Pd(1)–P(2)	91.18(9)	C(1)–Pd(1)–P(1)	85.8(1)
O(3)–Pd(1)–P(1)	94.11(9)	P(2)–Pd(1)–P(1)	174.66(4)
C(33)–P(2)–Pd(1)	118.3(1)	C(27)–P(2)–Pd(1)	112.6(2)
C(22)–P(2)–Pd(1)	112.4(2)	C(11)–P(1)–Pd(1)	110.0(2)
C(17)–P(1)–Pd(1)	118.6(2)	C(5)–P(1)–Pd(1)	114.1(2)
C(17)–N(1)–C(18)	117.0(6)	C(22)–N(2)–C(23)	116.5(5)
C(1)–O(2)–C(2)	116.9(4)	C(3)–O(3)–Pd(1)	114.7(4)
O(1)–C(1)–O(2)	121.6(4)	O(1)–C(1)–Pd(1)	127.9(4)
O(2)–C(1)–Pd(1)	110.5(3)	O(4)–C(3)–O(3)	124.0(5)
O(4)–C(3)–C(4)	120.8(6)	O(3)–C(3)–C(4)	115.2(7)
C(21)–C(17)–N(1)	120.4(5)	C(19)–C(18)–N(1)	121.4(6)

As alluded to above, insertion into the M–C bond of an alkoxycarbonyl intermediate is a key step in one of the catalytic cycles proposed for the alkoxycarbonylation of terminal alkynes as depicted in Scheme 2. In an effort to elucidate the operation or otherwise of such a mechanism for the present complexes, reactions were performed with alkynes and followed by NMR spectroscopy and GC-MS.

The stoichiometric reaction of **4** and **5** with phenylacetylene gives the σ-alkynyl complexes $PdL_2(C{\equiv}CPh)(CF_3CO_2)$, **6**, and $PdL_2(C{\equiv}CPh)Cl$, **7**, in quantitative yield through simple metathesis of the methoxycarbonyl ligand. No reaction is

Table 6 Selected bond lengths (Å) and angles (°) for $Pd(Ph_2Ppy)_2(CH_3CO_2)Cl$

Pd(1)–C(35)	1.970(5)	Pd(1)–P(1)	2.3257(11)
Pd(1)–P(2)	2.3285(11)	Pd(1)–Cl(1)	2.4035(15)
P(1)–C(6)	1.824(5)	P(1)–C(1)	1.837(5)
P(1)–C(12)	1.806(5)	P(2)–C(18)	1.811(5)
P(2)–C(23)	1.828(4)	P(2)–C(29)	1.837(5)
O(1)–C(35)	1.185(5)	O(2)–C(35)	1.338(5)
O(2)–C(36)	1.458(6)	C(1)–C(5)	1.349(6)
C(1)–N(1)	1.335(6)	C(2)–N(1)	1.350(8)
C(18)–N(2)	1.401(6)	N(2)–C(22)	1.412(6)
C(35)–Pd(1)–P(1)	87.85(12)	C(35)–Pd(1)–P(2)	89.07(12)
P(1)–Pd(1)–P(2)	174.59(4)	C(35)–Pd(1)–Cl(1)	176.49(13)
P(1)–Pd(1)–Cl(1)	90.09(4)	P(2)–Pd(1)–Cl(1)	93.20(4)
C(12)–P(1)–C(6)	103.2(2)	C(12)–P(1)–C(1)	108.9(2)
C(6)–P(1)–C(1)	102.1(2)	C(12)–P(1)–Pd(1)	113.08(16)
C(1)–P(1)–Pd(1)	118.65(14)	C(1)–P(1)–Pd(1)	110.05(16)
C(18)–P(2)–Pd(1)	115.00(14)	C(23)–P(2)–Pd(1)	118.50(15)
C(29)–P(2)–Pd(1)	112.21(15)	C(35)–O(2)–C(36)	115.2(2)
O(1)–C(35)–O(2)	122.9(4)	O(1)–C(35)–Pd(1)	127.8(4)
O(2)–C(35)–Pd(1)	109.3(3)		

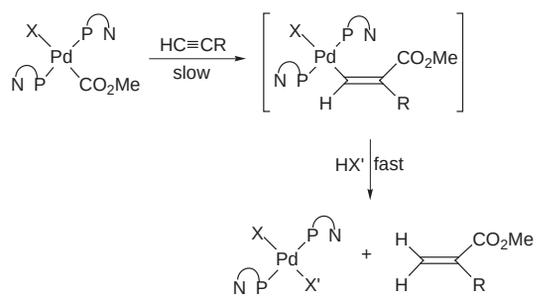


Scheme 2

observed for **4** or **5** at room temperature, complex **6** is formed after heating at 70 °C for four hours and **7** after six hours at the same temperature. Both reactions have been followed spectroscopically. Throughout the course of the reactions, ^{31}P NMR spectra show signals for the starting material and product only, and ^{1}H spectra after completion of the reactions show the clean formation of the σ-alkynyl complexes with no signals due to carbomethoxy alkenyl products. With respect to the parental alkoxycarbonyl complexes, the ^{1}H NMR spectra of **4** and **5** show new signals at δ 6.45 (doublet) and 6.65 (multiplet) that are assignable to the *ortho* and *meta* protons of the phenylacetylide ligand. The ν(C≡C) stretch occurs at 2098 cm^{-1} in the infrared spectrum, shifted only slightly from its position in free phenylacetylene. Elimination of the methoxycarbonyl ligand probably occurs *via* the formation of methyl formate, as indicated by the presence of an additional signal at δ 3.4 (CH_3, in C_6D_6) in the ^{1}H spectra: the formate resonance was lost under the mass of aromatic peaks around δ 8, however, spiking the solution with commercial methyl formate enhanced the peak at δ 3.4. When phenylacetylene is used in large excess (×25) complex **6** is formed after *ca.* 1 h at 70 °C. Further heating results in the decomposition of phenylacetylene to polymerised products and vinyl phosphonium salts identified by the large coupling constants of the vinyl hydrogens with the phosphorus atom. The reaction of the acetato-complex **1** with phenylacetylene gives a mixture of products that have not been identified.

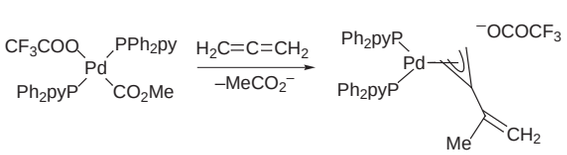
When **4** was combined in 1 : 5 : 7.5 ratio with phenylacetylene and methanol in d_6-benzene and carbon monoxide bubbled through the solution for five minutes, ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of the reaction solution (after stirring for 30 minutes at room temperature) indicated the clean formation of the alkynyl complex $Pd(Ph_2Ppy)_2(C{\equiv}CPh)(O_2CCF_3)$, **6**. Other signals in the ^{1}H NMR spectrum were from unreacted phenylacetylene, while no signals due to a β-unsaturated methylester were observed. When the reaction was repeated under 30 psi pressure of carbon monoxide, all phenylacetylene was converted regioselectively to methyl 2-phenylpropenoate. $Pd(Ph_2Ppy)_2(CO_2Me)Cl$ exhibits the same reactivity as **4**; under carbon monoxide at atmospheric pressure only the corresponding σ-alkynyl complex is formed but at 30 psi CO, catalysis is induced and methyl 2-phenylpropenoate is formed selectively.

The above observations show that a simple ligand metathesis is taking place during the reaction of complexes **4** and **5** with terminal alkynes, without any evidence to suggest initial formation of the insertion product of Scheme 3. This reactivity is



Scheme 3

akin to that of related platinum complexes reported by Clarke and Werner who prepared complexes of the type $[Pt(PPh_3)_2(CO)(C{\equiv}CR')][BF_4]$ (R′ = Me, Ph, CO_2Me) from $[Pt(PPh_3)_2(CO)(CO_2R)][BF_4]$ and the appropriate alkyne.[11] However, since methyl 2-phenylpropenoate is the exclusive product from catalytic reactions using **4** and **5** under 30 psi pressure of CO, another palladium species must be formed *in situ* at these pressures to induce catalysis. The exact nature of this catalyst remains elusive, but it is clear that the Pd–C≡CPh group does not incorporate CO and is probably not present in the active catalyst. Unlike reactions with PPh_3 based catalysts, catalytic systems based on Ph_2Ppy are poisoned by propadiene. This incongruity prompted an investigation of the reactivity of propadiene with the alkoxycarbonyl complexes reported here. Heating $Pd(Ph_2Ppy)_2(CO_2Me)(O_2CCF_3)$ with allene for two hours at 60 °C leads to the unusual π-allyl complex **8** (Scheme 4). Prolonged heating gives the palladium dimer,



Scheme 4

$Pd_2(\mu\text{-}Ph_2Ppy)_2(O_2CCF_3)_2$. A π-allyl carboxylate complex, from insertion of allene into the Pd–carbonyl bond, was not observed.

Crystals of **8** suitable for structural determination were obtained from CH_2Cl_2/petroleum ether. The molecular structure of **8** with the adopted numbering scheme is shown

Table 7 Selected bond lengths (Å) and angles (°) for $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3)=CH_2\}][O_2CCF_3]$

Pd(1)–C(35)	2.164(3)	Pd(1)–C(37)	2.165(3)
Pd(1)–C(36)	2.205(3)	Pd(1)–P(1)	2.3189(9)
Pd(1)–P(2)	2.319(1)	P(1)–C(7)	1.813(4)
C(35)–C(36)	1.403(5)	C(36)–C(37)	1.412(5)
C(36)–C(38)	1.502(5)	C(38)–C(40)	1.327(6)
C(38)–C(39)	1.477(6)	C(41)–C(42)	1.536(7)
C(35)–Pd(1)–C(37)	66.0(1)	C(35)–Pd(1)–C(36)	37.5(1)
C(37)–Pd(1)–C(36)	37.7(1)	C(35)–Pd(1)–P(1)	156.7(1)
C(37)–Pd(1)–P(1)	91.4(1)	C(36)–Pd(1)–P(1)	120.1(1)
C(35)–Pd(1)–P(2)	96.1(1)	C(37)–Pd(1)–P(2)	162.0(1)
C(36)–Pd(1)–P(2)	127.4(1)	P(1)–Pd(1)–P(2)	106.57(3)
C(7)–P(1)–Pd(1)	114.8(1)	C(13)–P(1)–Pd(1)	105.4(1)
C(1)–P(1)–Pd(1)	122.6(1)	C(24)–P(2)–Pd(1)	116.7(1)
C(30)–P(2)–Pd(1)	112.2(1)	C(18)–P(2)–Pd(1)	112.8(1)
C(36)–C(35)–Pd(1)	72.9(2)	C(35)–C(36)–C(37)	113.7(4)
C(35)–C(36)–C(38)	123.3(4)	C(37)–C(36)–C(38)	121.4(4)
C(35)–C(36)–Pd(1)	69.7(2)	C(37)–C(36)–Pd(1)	69.6(2)
C(38)–C(36)–Pd(1)	117.8(3)	C(36)–C(37)–Pd(1)	72.7(2)
C(40)–C(38)–C(39)	121.4(5)	C(40)–C(38)–C(36)	120.6(4)
C(39)–C(38)–C(36)	118.0(4)	O(2)–C(41)–O(1)	131.4(5)

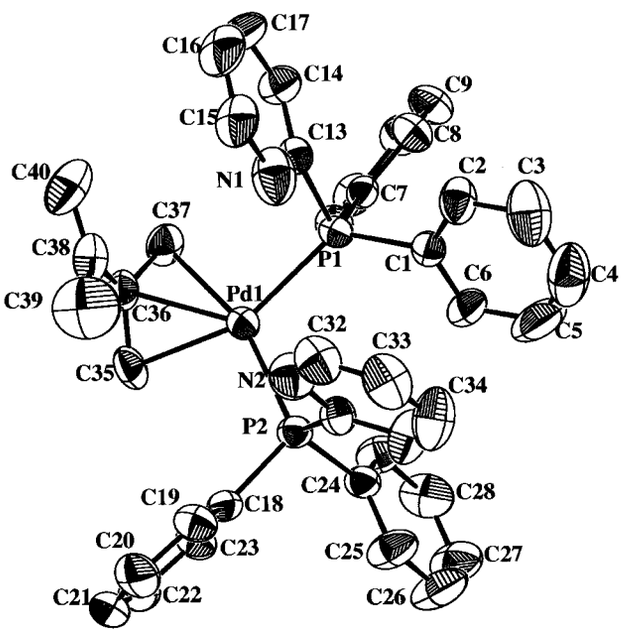


Fig. 3 Molecular structure of the $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3)\text{-}CH_2\}]^+$ cation in **8**.

in Fig. 3. Details of data collection are given in Table 4 with selected bond lengths and angles shown in Table 7. The complex may be described as square planar at the palladium atom, but, as is typical in complexes of this type, distortions from the ideal are significant, due in large part to the small bite angle of the allyl group as defined by the C(35)–Pd–C(37) value of 66.0(1)°, and the expanded P–Pd–P angle of 106.57(3)°. The maximum deviation from the plane defined by the Pd, two phosphorus donors and the terminal carbons is small (0.057 Å). The allyl ligand is symmetrically bonded to the palladium atom through the terminal carbons, the Pd–C bond distances being 2.164(3) and 2.165(3) Å, respectively. The central carbon atom (C_{36}) lies 0.163 Å below the P–Pd–P plane and has a slightly longer Pd–C bond length of 2.205(3) Å. The allyl ligand is strictly planar and forms an angle of 109.25° with the coordination plane. All these features of the coordinated allyl group compare well with published data.[12] The Pd–P bond distances of 2.319(1) Å are unexceptional.

The two hydrogens of the terminal methylene groups of the coordinated allyl ligand are chemically and magnetically distinct being defined as *syn* and *anti* in accord with established protocol. The two types of proton are readily distinguished by ^{1}H NMR where two broad signals are observed at δ 3.93 (H*syn*) and δ 3.16 (H*anti*) in the spectrum of **8**. Their broad appearance may reflect some unresolved $^3J_{PH}$ coupling which has been observed in similar systems with platinum. Each proton of the non-coordinated vinyl group gives a separate singlet at δ 5.23 and 5.17, respectively. The methyl group resonates at δ 1.57. In the infrared spectrum, the asymmetric CO stretch, ν(C=O), of the $CF_3CO_2^-$ ligand occurs at 1674.5 cm^{-1}, in accord with the ionic structure of **8**.

Insertion of allene into the Pd–allyl function has been observed previously by Hughes and Powell,[13] where the predominant product was from the coupling of the central C(2) carbon of the allene and a terminal carbon of the coordinated allyl. However, at high concentrations, reasonable yields of the symmetric C(2)–C(2) coupled product, which formed diallyl bridges between two palladium centres, were obtained. Similar compounds of platinum have been synthesised by propadiene insertion into Pt–σ-alkenyl bonds.[14] In addition, allene insertions into Pd–Cl bonds have been shown to give chloride substituted allyls or methoxy derivatives when performed in the presence of methanol.[15] In the presence of readily replaced ligands (weak donors), coordination of allene may occur after the formation of a σ-allyl complex, and this may insert to give compounds such as **8**.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone under nitrogen, except for toluene (sodium), methanol (calcium hydride) and dichloromethane (calcium hydride). Deuteriated solvents were dried and stored over molecular sieves (4 Å) and degassed before use using freeze–thaw techniques. All other chemicals were used as supplied (Aldrich) without further purification. ^{1}H and ^{13}C NMR were recorded on a Bruker DPX400 spectrometer operating at 400.13 MHz and 100 MHz, respectively. ^{31}P NMR spectra were acquired using a JEOL FX90Q spectrometer at 36.2 MHz and referenced to 85% H_3PO_4. Infrared spectra were recorded as KBr discs on a Nicolet 510 FT-IR spectrophotometer. The compounds $PdCl_2(Ph_2Ppy)_2$[16] and propadiene[17] were prepared by literature procedures.

trans-$Pd(Ph_2Ppy)_2(CO_2CH_3)(OAc)$ 1

Carbon monoxide was passed slowly through a solution of $Pd(OAc)_2$ (0.2 g, 0.89 mmol) and Ph_2Ppy (0.5 g, 1.9 mmol) in methanol (20 ml) at ambient pressure over a period of 2 hours. The resultant solution was concentrated *in vacuo* to *ca.* 5 ml, and the precipitated white solid collected, washed with diethyl ether (3 × 20 ml) and air-dried. Colourless crystals were obtained by slow diffusion of petroleum ether (bp 40–60 °C) into a toluene solution of the crude solid. Yield 0.47 g, 70% (Found: C, 60.9; H, 4.7; N, 3.7. Calc. for $C_{38}H_{34}O_4N_2P_2Pd$: C, 60.77; H, 4.56; N, 3.50%). Following isolation of **1**, a mixture of crystals of **1** and red crystals of $Pd_2(Ph_2Ppy)_2(OAc)_2$ was obtained by slow diffusion of a 1 : 1 mixture of diethyl ether and petroleum ether into the mother liquor.

Complexes **2** and **3** were prepared by an analogous procedure using the appropriate alcohol as solvent. *trans*-$Pd(Ph_2Ppy)_2(CO_2Et)(OAc)$ **2**. Yield = 0.46 g, 68% (Found: C, 61.0; H, 4.7; N, 3.5. Calc. for $C_{39}H_{36}N_2O_4P_2Pd$: C, 61.20; H, 4.75; N, 3.66%). *trans*-$Pd(Ph_2Ppy)_2(CO_2i\text{-}Pr)(OAc)$ **3**. Yield = 0.42 g, 60% (Found: C, 61.2; H, 5.0; N, 3.2. Calc. for $C_{40}H_{38}N_2O_4P_2Pd$: C, 61.66; H, 4.92; N, 3.60%).

trans-$Pd(Ph_2Ppy)_2(CO_2CH_3)(CF_3CO_2)$ 4

In a glass pressure vessel $Pd(OAc)_2$ (0.2 g, 0.9 mmol), Ph_2Ppy (0.48 g, 1.8 mmol) and CF_3CO_2H (0.15 ml, 2.0 mmol) were

dissolved in methanol (10 ml) and carbon monoxide (50 psi) was immediately introduced to the solution. After 10 minutes a white solid had begun to precipitate. The reaction mixture was left stirring for a further hour, before the pressure was released and the solid collected, washed with diethyl ether (2 × 20 ml) and dried *in vacuo*. Yield = 0.51 g, 71% (Found: C, 56.7; H, 3.9; N, 3.5. Calc. for $C_{38}H_{31}F_3O_4N_2P_2Pd$: C, 56.69; H, 3.89; N, 3.48%). The mother liquor from the reaction contained small amounts of the monomeric and dimeric complexes $Pd(Ph_2Ppy)_2(CF_3CO_2)_2$ and $Pd_2(Ph_2Ppy)_2(CF_3CO_2)_2$.

trans-$Pd(Ph_2Ppy)_2(CO_2CH_3)Cl$ 5

To a stirred suspension of $Pd(Ph_2Ppy)_2Cl_2$ (0.22 g, 0.31 mmol) in methanol (5 ml) under an atmosphere of carbon monoxide was added a solution of sodium methoxide (17 mg, 0.31 mmol) in methanol (10 ml). Carbon monoxide was then bubbled through the solution for a period of two hours. Precipitation of the white product was completed by the addition of diethyl ether. Complex **5** was extracted from the crude solid with CH_2Cl_2 which was evaporated *in vacuo* and the resultant powder crystallised from CH_2Cl_2/petroleum ether (bp 40–60 °C). Yield = 0.12 g, 52% (Found: C, 59.2; H, 4.1; N, 3.7. Calc. for $C_{36}H_{31}ClN_2O_2P_2Pd$: C, 59.44; H, 4.30; N, 3.88%).

Alternatively complex **5** was obtained from $[Pd(Ph_2Ppy)_2Cl][OTf]$, by following the same procedure as above.

trans-$Pd(Ph_2Ppy)_2(C{\equiv}CPh)(O_2CCF_3)$ 6

Phenylacetylene (25 μl, 0.18 mmol) was added to a solution of $Pd(Ph_2Ppy)_2(CO_2Me)(O_2CCF_3)$ (0.1 g, 0.12 mmol) in toluene (40 ml) and the mixture heated at 70 °C for five hours. After reducing the volume by half, complex **6** was precipitated as a white solid by the addition of petroleum ether (bp 40–60 °C). Yield = 0.10 g, 93% (Found: C, 61.9; H, 4.1; N, 2.9. Calc. for $C_{44}H_{33}F_3O_2N_2P_2Pd$: C, 62.40; H, 3.93; N, 3.30%). The same procedure was followed to obtain *trans*-$Pd(Ph_2Ppy)_2(C{\equiv}CPh)Cl$, **7**, from $Pd(Ph_2Ppy)_2(CO_2Me)Cl$. Yield = 92 mg, 95% (Found: C, 64.7; H, 4.3; N, 3.5. Calc. for $C_{42}H_{33}ClN_2P_2Pd$: C, 65.55; H, 4.33; N, 3.64%).

$[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3){=}CH_2\}][O_2CCF_3]$ 8

Propadiene (1 g) was added to a solution of $Pd(Ph_2Ppy)_2(CO_2Me)(O_2CCF_3)$ (0.3 g; 0.41 mmol) in toluene (30 ml) and the reaction mixture heated at 65 °C for 15 hours. After evaporation of the solvent, the resulting oily compound was triturated with petroleum ether to give a yellow solid. Crystallisation from CH_2Cl_2/petroleum ether (bp 40–60 °C) gave yellow crystals of **8**. Yield = 0.30 g, 90%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.5. ^1H NMR ($CDCl_3$): δ 5.23 (br, s, 1H), 5.17 (br, s, 1H); 3.93 (br, s, 2H); 3.16 (br, s, 2H); 1.57 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 73.5 (br, $C_{terminal}$), 118.4 (s, $C(CH_3)CH_2$), 20.0 (s, $C(CH_3)CH_2$). IR (KBr disks, cm^{-1}): $\nu(CF_3CO_2)$ 1674.5 s, 1194.3 m, 1166.0 m, 1121.0 m, 1100.0 m.

Reactions of complexes 4 and 5 with phenylacetylene, methanol and CO, as monitored by NMR spectroscopy

Carbon monoxide was bubbled through a C_6D_6 (0.8 ml) solution of $Pd(Ph_2Ppy)_2(CO_2Me)(O_2CCF_3)$ (30 mg, 0.04 mmol), phenylacetylene (20 μl, 0.2 mmol) and methanol (12 μl, 0.3 mmol) for five minutes. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction solution showed complete conversion to $Pd(Ph_2Ppy)_2(C{\equiv}CPh)(O_2CCF_3)$ in addition to unreacted phenylacetylene.

$Pd(Ph_2Ppy)_2(CO_2Me)(O_2CCF_3)$ (0.25 g, 0.34 mmol), methanol (0.3 ml, 7.4 mmol) and phenylacetylene (0.4 ml, 3.4 mmol) were dissolved in C_6D_6 (2 ml) and a pressure of 30 psi of carbon monoxide applied. The solution was stirred at room temperature for 1 day. The ^1H NMR spectrum of the reaction mixture confirmed the complete conversion of phenylacetylene to methyl 2-phenylpropenoate. ^1H NMR (δ) of methyl 2-phenylpropenoate: 6.32 (s, C=CH_2), 5.67 (s, C=CH_2), 3.51 (s, CO_2Me).

$Pd(Ph_2Ppy)_2(CO_2Me)Cl$ (41 mg, 0.06 mmol), methanol (100 μl, 2.5 mmol) and phenylacetylene (30 μl, 0.27 mmol) were dissolved in $CDCl_3$ (0.8 ml) and 30 psi of carbon monoxide pressure applied. The solution was stirred for 18 h and the ^1H and $^{31}P\{^1H\}$ NMR spectra recorded. Petroleum ether was added to precipitate the palladium containing products and a sample from the supernatant solution was taken for GC-MS analysis (*m*/*z* 162, methyl 2-phenylpropenoate).

Crystallography

Single crystals of **1**, **5** and **8** suitable for X-ray diffraction analysis were mounted on glass fibres and data recorded at temperatures of 145, 150 and 293 K respectively. Data were collected on a Delft Instruments FAST TV area detector at the window of a rotating anode generator with a molybdenum target [(Mo-Kα) = 0.71069 Å], driven by MADNES[18] software using a procedure previously described.[19] Data reduction was performed using the program ABSMAD.[20] The structures were solved by heavy atom methods (SHELX-S)[21] and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL-93).[22] Non-hydrogen atoms were refined anisotropically with all hydrogens fixed in idealised positions and isotropic thermal parameters tied to the value of the parent atom. The weighting scheme used was $w = 1/[(2(F_o^2)]$ which gave satisfactory agreement analyses. The nitrogen atoms in the pyridyl rings were distinguished from the carbons by inspection of peak heights in the difference map, bond lengths and consideration of thermal ellipsoids. Data were corrected for absorption effects using the program DIFABS.[23] Diagrams were drawn with SNOOPI.[24]

CCDC reference number 186/1359.

See http://www.rsc.org/suppdata/dt/1999/1113/ for crystallographic files in .cif format.

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