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Condensation reactions of monomeric hydroxo palladium complexes with active methyl and methylene compounds†

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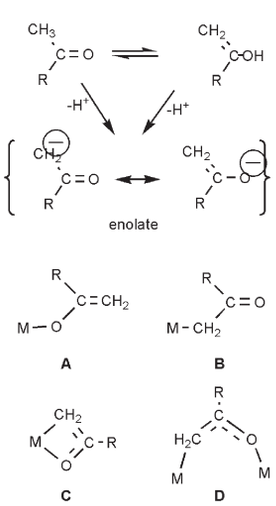
Heating a suspension of the monomeric hydroxo palladium complex of the type [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, Me_2bipy, phen or tmeda) in methylketone (acetone or methylisobutylketone) under reflux affords the corresponding ketonyl palladium complex [Pd(N–N)(C_6F_5)(CH_2COR)]. On the other hand, the reaction of the hydroxo palladium complexes [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, phen or tmeda) with diethylmalonate or malononitrile yields the C-bound enolate palladium complexes [Pd(N–N)(CHX_2)(C_6F_5)] (X = CO_2Et or CN), and the reaction of [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy or phen) with nitromethane gives the nitromethyl palladium complexes [Pd(N–N)(CH_2NO_2)(C_6F_5)]. [Pd(tmeda)(C_6F_5)(OH)] catalyses the cyclotrimerization of malononitrile. The crystal structures of [Pd(bipy)(C_6F_5)(CH_2COMe)]·½Me_2CO, [Pd(tmeda)(C_6F_5){$CH(CO_2Et)_2$}], [Pd(tmeda)(C_6F_5){$CH(CN)_2$}] and [Pd(tmeda)(C_6F_5)(CH_2NO_2)]·½CH_2Cl_2 have been established by X-ray diffraction.

Introduction

Palladium has been widely used for assisting the reactivity of enolate species,[1–9] but the number of isolated and well-characterized complexes is rather limited. Oxygen-bound enolates (type A in Scheme 1) are common for early transition metals, but, as expected for a late transition metal, enolates prefer to coordinate to palladium either through the carbon atom (type B; Scheme 1) [10–18] or in the chelating η^3-oxoallyl fashion (type C; Scheme 1).[19–22] Bridging C,O–enolates have also been isolated.[11–13,23] O-bound and C-bound enolates may be alternatively named as enolate and ketonyl complexes, respectively.



Scheme 1

Palladium enolates can be prepared by oxidative addition of haloketones to a Pd(0) complex[13,16,17,23,24] and Pt–methyl enolate complexes have also been prepared by reacting acetone with hydroxo complexes.[25–28] In particular, bridging C,O-enolates were prepared[11] from acetone and di-μ-hydroxo complexes >Pd(μ-$OH)_2$Pd< and the reaction of the Pd(μ-$CH_2C(R)O)_2$Pd-type complexes with a monodentate ligand afforded the acetonyl complexes >Pd{$CH_2C(O)R$}L. These acetonyl complexes should directly be formed by using a monohydroxo complex as precursor. Recently abstraction of the α-proton of a carbonyl compound by a hydroxo palladium complex has been reported to be a key for the synthetically useful enantioselective catalysis.[29] We have recently described[30,31] the synthesis of monomeric hydroxo palladium(II) complexes of the type [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, Me_2bipy, phen or tmeda) and their reactions with CO or SO_2 in methanol at room temperature to yield the corresponding methoxy carbonyl or alkylsulfito complexes [Pd(N–N)(C_6F_5)(X)] (X = CO_2Me or SO_3Me)]. The reactions of the monomeric hydroxo complexes [Pd(N–N)(C_6F_5)(OH)] with some active methyl (CH_3COR or CH_3NO_2) and methylene (CH_2X_2) (X = CO_2Et or CN) compounds have now been examined and we report herein the first crystal structure of a dicyanomethanide–palladium complex (3D Search using the Cambridge Structural Database, CSD version 5.25, April 2004 release), together with the crystal structures of an acetonyl–palladium complex, a nitromethyl–palladium complex, and a dimethyl malonate–palladium complex.

Results and discussion

Ketonyl palladium complexes 1–6

On heating a suspension of the hydroxo complex [Pd(N–N)-(C_6F_5)(OH)] (N–N = bipy, Me_2bipy or phen) in methylketone (acetone or methylisobutylketone) under reflux the β-carbonylmethyl palladium complexes **1**–**6** are formed with the concomitant release of water (Scheme 2)**.** Complexes **1**–**6** are all air-stable solids and the thermal analysis shows that they decompose above 220 °C in a dynamic N_2 atmosphere. The IR spectra show the characteristic absorptions of the C_6F_5 group[32] at 1630, 1490, 1450, 1050, 950 and a single band at *ca.* 800 cm^{-1} which is derived from the so-called X-sensitive mode[33] in C_6F_5-halogen molecules, which is characteristic of the presence of only one C_6F_5 group in the coordination sphere of the palladium atom and behaves like a ν(M–C) band.[34–36] The carbonyl stretching frequencies for these β-carbonylmethyl–palladium complexes fall in the range 1635–1615 cm^{-1}. These values are similar to those found in related monomeric β-carbonylmethyl–palladium

† Electronic supplementary information (ESI) available: Table S1: ^1H and ^{19}F NMR data. See http://www.rsc.org/suppdata/dt/b4/b409942g/

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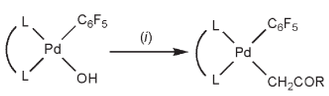
complexes[6,10–14] and are indicative of the absence of interaction between the carbonyl group and the palladium atom. The full list of ^{1}H and ^{19}F NMR data is given in the ESI† (Table S1) and relevant data are found in the Experimental section. The characteristic resonances of the neutral ligands bipy, Me_2bipy, phen and tmeda are observed in the ^{1}H NMR spectra within the ranges found for related compounds.[30,37–39] The signals in the range δ 2.54–2.72 are assignable to the methylene protons for complexes **1**–**6**. Complexes **1**, **3** and **5** show also a resonance at δ 1.97–1.86 for the methyl protons of the acetonyl ligand, whereas complexes **2**,**4** and **6** show resonances at δ 1.87 and 0.78 for the methylidene and methyl protons, respectively, of the Bu^{i} group. The ^{19}F NMR spectra of complexes **1**–**6** reveal the presence of a freely rotating pentafluorophenyl ring which gives three resonances (in the ratio 2 : 2 : 1) at *ca.* −116.0, −160.5 and −163.0 for the *o*-, *m*- and *p*-fluorine atoms, respectively. In the $^{13}C\{^{1}H\}$ NMR spectrum of complex **1**, resonances due to the chelating ligand, together with those of the methyl (δ 29.6) and the methylene (δ 25.0) of the acetonyl group were observed. No carbonyl carbon resonance could be observed probably due to the low solubility of this complex.



1	L_2 = bipy	R = Me
2	L_2 = bipy	R = Bu^{t}
3	L_2 = Me_2bipy	R = Me
4	L_2 = Me_2bipy	R = Bu^{t}
5	L_2 = phen	R = Me
6	L_2 = phen	R = Bu^{t}

Scheme 2 *Reagents and conditions*: (i) MeCOR/$-H_2O$, 5–7 h, reflux.

Fig. 1 shows the X-ray structure of complex **1**·½Me_2CO, with selected bond lengths and bond angles listed in Table 1. Complex **1**·½Me_2CO contains a palladium atom located in a distorted square planar environment, formed by the two nitrogen atoms of the chelating bipy ligand, the C_{ipso} of the C_6F_5 ring and one carbon atom of the acetonyl ligand. The Pd–N bond distances (Pd(1)–N(1), 2.097(2) Å; Pd(1)–N(2), 2.102(2) Å) are longer than those observed in the related complex [Pd(bipy)(C_6F_5)(OOCPh)]·$CHCl_3$.[40] The chelate angle N(1)–Pd–N(2) (78.70(8)°) is smaller than that found in [Pd(bipy)(C_6F_5)(OOCPh)]·$CHCl_3$.[40] The distance Pd–C(17) (2.078(2) Å) is shorter than that found in [Pd($AsPh_3$)(C_6F_5){$CH_2C(O)CH_3$}(^{t}BuNC)] (2.111(4) Å)[11] but longer than that in [Pd_2{$CH_2C(O)CH_3$}(μ-Cl)$_2$(tetrahydrothiophene)$_2$] (2.050(3) Å).[12] The length of the carbon–oxygen double bond (1.229(3) Å) is similar to that found in [Pd($AsPh_3$)(C_6F_5){$CH_2C(O)CH_3$}(^{t}BuNC)] (1.230(5) Å).[11] The enolate ligand is nearly perpendicular to the mean coordination plane (dihedral angle 71.7°); the same conformation is found in [Pd($AsPh_3$)(C_6F_5){$CH_2C(O)CH_3$}(^{t}BuNC)][11] or in [Pd(CH_2COPh)Cl(PPh_3)$_2$].[13] In complex **1**·½Me_2CO there is a stack of inversion related molecules along the *b*-axis direction with π–π interactions between pyridine rings of bipyridine ligands.[41] As can be seen in Fig. 2 there is a slipped packing with a deviation of the centre–centre line of the perpendicular of the plane of 16.4°, the interplanar distance is 3.47 Å. The are also CH···O and CH···F bonds links (2.516–2.594 Å).

Malonate–palladium complexes 7–9

The reaction of the corresponding hydroxo complex [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, phen or tmeda) with diethylmalonate yields the malonate palladium complexes **7**–**9** shown in Scheme 3. Complexes of malonate anions are likely intermediates in the recently developed palladium-catalyzed arylations of malonates[7,8] and C–C bond-forming reductive elimination from aryl palladium(II) complexes of malonate anions has been very recently reported.[9] The IR spectra of complexes **7**–**9** show a very strong carbonyl absorption at *ca.* 1720 cm^{-1},

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**·½Me_2CO

Pd(1)–C(11)	2.009(2)	C(11)–Pd(1)–C(17)	87.84(10)
Pd(1)–C(17)	2.078(2)	C(11)–Pd(1)–N(1)	174.97(9)
Pd(1)–N(1)	2.097(2)	C(17)–Pd(1)–N(1)	96.85(9)
Pd(1)–N(2)	2.102(2)	C(11)–Pd(1)–N(2)	96.77(9)
C(18)–O(1)	1.229(3)	C(17)–Pd(1)–N(2)	173.28(9)
C(17)–C(18)	1.468(4)	N(1)–Pd(1)–N(2)	78.70(8)
C(18)–C(19)	1.517(4)	C(18)–C(17)–Pd(1)	107.22(17)

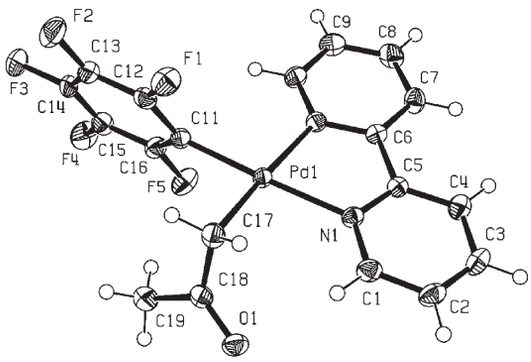


Fig. 1 ORTEP of complex **1**·½Me_2CO showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

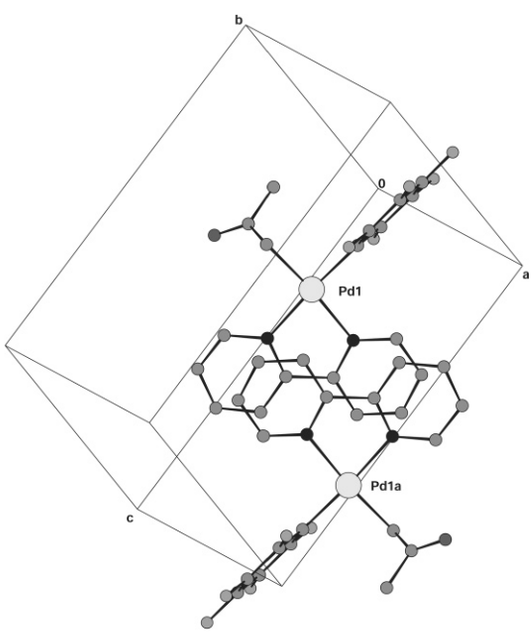
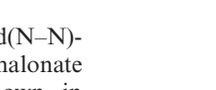


Fig. 2 π–π Interactions in complex **1**·½Me_2CO. Symmetry code: (a) 1 − *x*, −*y*, 1 − *z*.

which further confirms the presence of the Pd–C σ-bond formation.[42,43] The ^{1}H NMR spectra show the methine proton of the malonate ligand as a singlet at *ca.* δ 3.6–3.0. This value is close to the δ 4.0–4.4 range for related C-bonded complexes and differs significantly from the O-bonded range (δ 4.7–5.4).[42] In the $^{13}C\{^{1}H\}$ NMR spectra the CH resonance is observed at δ 22.5 (for **7**), 22.7 (for **8**) or 26.4 (for **9**).



7	L_2 = bipy	X = CO_2Et
8	L_2 = phen	X = CO_2Et
9	L_2 = tmeda	X = CO_2Et
10	L_2 = bipy	X = CN
11	L_2 = phen	X = CN
12	L_2 = tmeda	X = CN

Scheme 3 *Reagents*: $CH_2X_2/-H_2O$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **9** (mean values for the two molecules in the asymmetric unit)

Pd(1)–C(1)	2.001(4)	C(1)–Pd(1)–C(13)	89.4(2)
Pd(1)–C(13)	2.094(4)	C(1)–Pd(1)–N(2)	92.4(2)
Pd(1)–N(2)	2.145(4)	C(13)–Pd(1)–N(2)	177.2(2)
Pd(1)–N(1)	2.161(4)	C(1)–Pd(1)–N(1)	176.1(2)
		C(13)–Pd(1)–N(1)	94.0(2)
		N(2)–Pd(1)–N(1)	84.4(2)

The structure of **9** is shown in Fig. 3 and selected bond lengths and bond angles are given in Table 2. There are two independent molecules which differ in the orientation of one CO_2Et group. The coordination around Pd is distorted square planar. The different Pd–N (Pd–N(1), 2.161(4) Å; Pd–N(2), 2.145(4) Å) distances are in agreement with the higher *trans* influence of the C_6F_5 group compared to the malonate ligand. The Pd–C(13) bond distance (2.094(4) Å) is similar to that observed in the previously reported bis(diethylmalonate-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) complex.[42] The angles at the central carbon atom of the malonate ligand indicate sp^3-hybridization of carbon. The Pd–C_6F_5 bond length (2.001(4) Å) is in the range found in the literature for pentafluorophenyl–palladium complexes. The chelate angle N(1)–Pd–N(2) (84.4(2)°) is similar to that found in [Pd(tmeda)(C_6F_5)(CO_2Me)].[30]

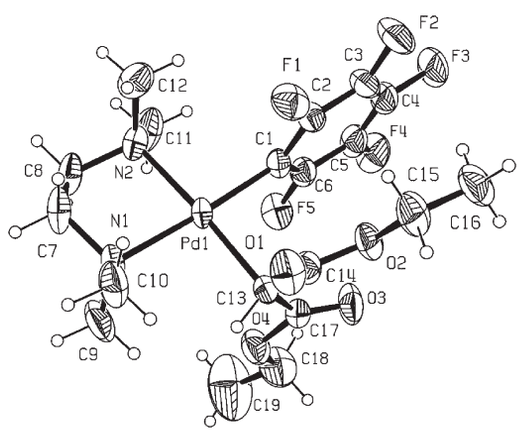


Fig. 3 ORTEP of complex **9** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

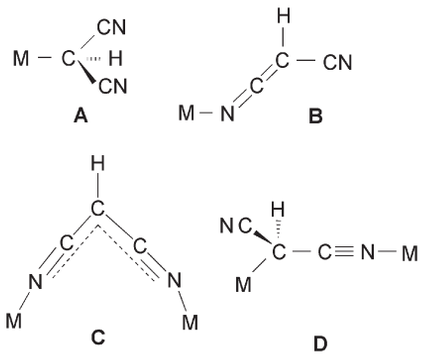
Dicyanomethanide–palladium complexes 10–12

The reaction of [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, phen or tmeda) with malononitrile yields the dicyanomethanide–palladium complexes **10**–**12** (Scheme 3). The dicyanomethanide anion, $[CH(CN)_2]^-$, resulting from the deprotonation of malononitrile, may coordinate to metal centres either by the nitrogen or the carbon atom, depending on the hard–soft character of the metal ion, and examples of both possibilities (Scheme 4), **A** (dicyanomethyl–metal linkage) and **B** (monocyanoketimine structure), are found in the literature.[28,44–49] A third coordination mode is as bidentate N,N-bonded ligand bridging two metal atoms as found in $[\{Ni(C_6F_5)_2(\mu\text{-}NCCHCN)\}_2]^{2-}$ (**C**).[50] The malonitrilate anion also can act as bidentate C,N–bonded ligand as observed in $[\{Pd(C_6F_5)_2(\mu\text{-}CH(CN)CN)\}_2]^{2-}$ (**D**).[51] The IR spectra of complexes **10**–**12** show a sharp ν(CN) band at 2210–2220 cm^{-1}, which is similar to the value of 2225 cm^{-1} found in the related C-bonded[28,45] complexes [(Tp^{Me2})(py)Pd{$CH(CN)_2$}] and [(dppe)PtMe{$CH(CN)_2$}], whereas N-bonded dicyanoketeniminato complexes containing the unit M–N=C=CH(CN) show[44,45] a broad, intense ν(CN) band in the range 2120–2150 cm^{-1}.

The structure of **12** is shown in Fig. 4 and selected bond lengths and angles in Table 3. The different Pd–N (Pd–N(2), 2.1511(13) Å; Pd–N(1), 2.1182(13) Å) distances are in agreement with the higher *trans* influence of the C_6F_5 group compared to the dicyanomethanide ligand. The angles at

Table 3 Selected bond lengths (Å) and angles (°) for complex **12**

Pd(1)–C(1)	2.0078(15)	C(1)–Pd(1)–C(7)	89.20(6)
Pd(1)–C(7)	2.0877(16)	C(1)–Pd(1)–N(1)	91.75(6)
Pd(1)–N(1)	2.1182(13)	C(7)–Pd(1)–N(1)	179.02(6)
Pd(1)–N(2)	2.1511(13)	C(1)–Pd(1)–N(2)	176.33(5)
		C(7)–Pd(1)–N(2)	94.40(6)
		N(1)–Pd(1)–N(2)	84.64(5)



Scheme 4

the central carbon atom of malononitrilate (108.9–111.0°) indicate sp^3-hybridization of carbon. The Pd–C(7) bond distance (2.0877(16) Å) is shorter than that observed in the previously reported $[Pd_2(C_6F_5)_4\{\mu\text{-}CH(CN)CN\}_2]^{2-}$ (2.191(7) Å).[51] The $C(CN)_2$ moiety is planar with maximum deviations of 0.008(1) Å [C(8)] and 0.006(1) Å [C(7)]. Both nitrile groups are linear, the corresponding angles C(7)–C(9)–N(4) and C(7)–C(8)–N(3) are 178.88(19) and 178.87(18)°, respectively. The C–N distances (1.148(2) and 1.150(2) Å) are similar to those found in [Co(salpn){$CH(CN)_2$}(py)] (1.16(2) and 1.14(2) Å).[52]

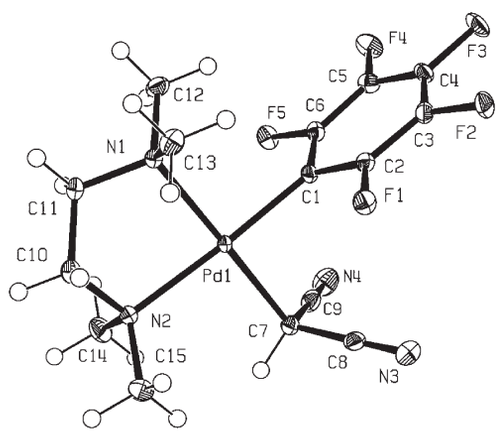
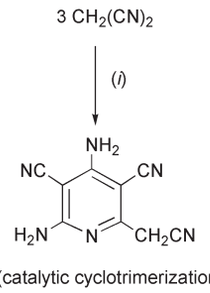


Fig. 4 ORTEP of complex **12** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the course of our research into the chemistry of $[NBu_4]_2[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]$-type complexes (M = Ni, Pd, Pt),[53] we found that the nickel and palladium complexes can be used as efficient catalysts for the cyclotrimerization of malononitrile.[50,51] Similarly, catalytic amounts of the mononuclear hydroxo palladium complex [Pd(tmeda)(C_6F_5)(OH)] in wet toluene also effect the cyclotrimerization of malononitrile, leading to 4,6-diamino-2-cyanomethyl-3,5-pyridinedicarbonitrile (Scheme 5), the so-called trimer I of malononitrile.[54] From a 1 : 100 molar mixture of [Pd(tmeda)(C_6F_5)(OH)] : malononitrile in boiling wet toluene the cyclic trimer is isolated in 35% yield. The relevant data are listed in the Experimental section, and are identical with those previously reported.[50,55]

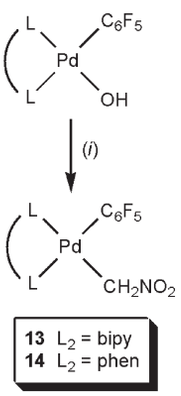
Nitromethyl palladium complexes 13 and 14

On heating a suspension of the corresponding hydroxo palladium complex [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy or phen)



Scheme 5 *Reagents and conditions*: (i) [Pd(tmeda)(C_6F_5)(OH)], wet toluene, 6 h, reflux.

in nitromethane under reflux the nitromethyl–palladium complexes **13** and **14** are obtained (Scheme 6). The nitromethyl complexes show $\nu(NO_2)$ in the expected region[26,28] of the IR spectrum (Experimental section). The methylene proton resonance is observed at δ 4.9–4.7[26,56,57] and the $^{13}C\{^1H\}$ NMR spectrum of **13** shows the CH_2 resonance at δ 22.4.



Scheme 6 *Reagents and conditions*: (i) $MeNO_2/-H_2O$, 3–4 h, reflux.

Fig. 5 shows the X-ray structure of complex **13**·½CH_2Cl_2, with selected bond lengths and bond angles listed in Table 4. The metal atom shows a distorted square planar geometry. The different Pd–N (Pd(1)–N(1), 2.102(2) Å; Pd(1)–N(2), 2.073(2) Å) distances are in agreement with the higher *trans* influence of the C_6F_5 group compared to the nitromethyl ligand. The chelate angle N(1)–Pd–N(2) (79.05(9)°) is higher than that found in complex **1**·½Me_2CO. The CH_2NO_2 group is characterized by the Pd–C(17) distance and a N(3)–C(17)–Pd angle of 2.060(3) Å and 110.7(2)° (sp^3 hybridization for the C atom), respectively. These values are shorter than those found in $[Pd(dppp)(tmphen)(CH_2NO_2)]^+$ and higher than those of $[Pd(phen)_2(CH_2NO_2)]^+$.[56]

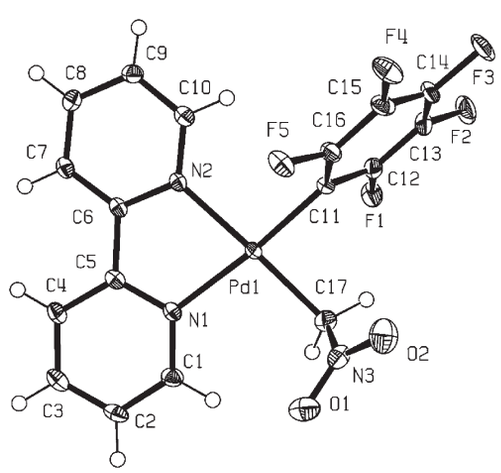


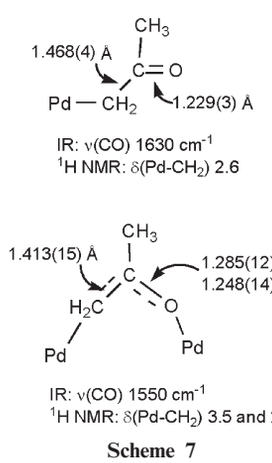
Fig. 5 ORTEP of complex **13**·½CH_2Cl_2 showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 4 Selected bond lengths (Å) and angles (°) for complex **13**·½CH_2Cl_2

Pd(1)–C(11)	2.003(3)	C(11)–Pd(1)–C(17)	87.11(12)
Pd(1)–C(17)	2.060(3)	C(11)–Pd(1)–N(2)	96.22(10)
Pd(1)–N(1)	2.102(2)	C(17)–Pd(1)–N(2)	173.71(11)
Pd(1)–N(2)	2.073(2)	C(11)–Pd(1)–N(1)	173.64(10)
		C(17)–Pd(1)–N(1)	98.01(11)
		N(1)–Pd(1)–N(2)	79.05(9)
		N(3)–C(17)–Pd(1)	110.7(2)

Conclusion

The acid–base reaction between [Pd(N–N)(C_6F_5)(OH)] and methyl ketones is a convenient method for the preparation of C-bonded enolate–palladium complexes. Previous results recently reported by us[11] showed that the di-μ-C,O-enolate complex [(N–N)(C_6F_5)Pd{μ-$CH_2C(R)O$}Pd(C_6F_5)(N–N)] is formed when the starting hydroxo complex is [(N–N)(C_6F_5)Pd(μ-OH)$_2$Pd(C_6F_5)(N–N)], because the vacant site at the palladium atom is occupied by the oxygen atom of the C-bound enolate. However, the carbophilic nature of palladium(II) is manifested when the bridging C,O-enolate complex is treated with a donor ligand and the Pd{$(CH_2C(O)R$}L-type complex is formed. Some structural data of the terminal C-bound and bridging C,O-bound enolate are compared in Scheme 7. The shorter C–O distance in the C-bound enolate correlates with the higher wavenumber observed for ν(CO) and the lack of electron delocalization on the C-bound enolate results in a high-field shift of the CH_2 proton resonance. So the carbonyl stretching band and the methylene proton resonance may be used as criteria for distinguishing terminal C-bound enolate from bridging C,O-bound enolate. The nitromethyl–palladium complex is obtained by a similar acid–base reaction between nitromethane and the hydroxo–palladium complex. Although aqua–palladium complexes have been obtained by protonation of hydroxo–palladium complexes,[58] no intermediate aqua complex has been detected in the above reactions.



Scheme 7

C-Bound dicyanomethanide– and diethylmalonate–palladium complexes are readily obtained by reaction between [Pd(N–N)(C_6F_5)(OH)] and malononitrile or diethylmalonate, respectively. However, when malononitrile is reacted with a di-μ-hydroxo–palladium complex the C,N-bound malonitrilate complex >Pd{$CH(CN)CN$}Pd< is formed.[51] This behaviour of malonitrile towards terminal monohydroxo and bridging hydroxo palladium complexes is similar to that described above for methyl ketones. The deprotonation of dialkylmalonate by the di-μ-hydroxo palladium complex leads to the formation of the O,O′-bound malonate complex >Pd{$OC(OEt)CHC(OEt)O$} whereas the same reaction carried out with the monohydroxo palladium complex affords the C-bound dialkylmalonate complex Pd{$CH(CO_2Et)_2$}. The X-ray structural data indicate that in the chelating O,O′-bound malonate the methine

carbon atom is sp^2-hybridized and in the C-bound malonate it is sp^3-hybridized. There is again a correlation between these data and the corresponding IR and ^{1}H NMR data: νCO) 1720 cm^{-1} and δ(CH) 3.6–3.0 for C-bound malonate *vs.* ν(CO) 1620 cm^{-1} and δ(CH) 4.2 for chelating O,O′-bound malonate.

Experimental

Instrumental measurements

C,H,N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid sample under nitrogen flow (100 mL min^{-1}). The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ or $CFCl_3$ as standards, respectively. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets.

Materials

The compounds [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, Me_2bipy, phen or tmeda) were prepared as described elsewhere.[30]

Preparation of complexes [Pd(N–N)(C_6F_5)(CH_2COR)] (1–6)

A suspension of the corresponding hydroxo palladium complex [(N–N)Pd(C_6F_5)(OH)] (N–N = bipy, Me_2bipy or phen) (0.134 mmol) in methylketone (acetone or MeCOBu^t) (15 mL) was heated under reflux for 5–7 h to yield a solution and then partially concentrated under vacuum. On addition of hexane the white complexes **1**–**6** precipitated and were filtered off and air-dried. Complex **1** was heated in the oven for 24 h at 80 °C to remove solvated acetone. **1**: Yield 90% (Found: C, 46.9; H, 2.8; N, 5.6. $C_{19}H_{13}N_2F_5OPd$ requires C, 46.9; H, 2.7; N, 5.8%); mp 241 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1635, ν(Pd–C_6F_5) 780. ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 2 H, $PdCH_2$), 1.88 (s, 3 H, $COCH_3$). ^{19}F NMR ($CDCl_3$): δ −116.3 (d, 2F$_o$, J(F$_o$F$_m$) = 22.9 Hz), −160.4 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.5 (m, 2 F$_m$). **2**: Yield 65% (Found: C, 50.2; H, 3.4; N, 5.4. $C_{22}H_{19}N_2F_5OPd$ requires C, 50.0; H, 3.6; N, 5.3); mp 224 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1625, ν(Pd–C_6F_5) 785. ^{1}H NMR ($CDCl_3$): δ 2.57 (s, 2 H, $PdCH_2$), 2.13 (d, 2 H, CH_2CH, J(HH) = 6.9 Hz), 1.87 (m, 1 H, CH), 0.78 (d, 6 H, CHCH_3, J(HH) = 6.5 Hz). ^{19}F NMR ($CDCl_3$): δ −116.3 (d, 2F$_o$, J(F$_o$F$_m$) = 22.9 Hz), −160.5 (t, 1 F$_p$, J(F$_m$F$_p$) = 20.0 Hz), −162.7 (m, 2 F$_m$). **3**: Yield 96% (Found: C, 48.8; H, 3.2; N, 5.2. $C_{21}H_{17}N_2F_5OPd$ requires C, 49.0; H, 3.3; N, 5.4%); mp 257 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1635, ν(Pd–C_6F_5) 780. ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 2 H, $PdCH_2$), 2.45 (s, 3 H, Me_2bipy), 2.42 (s, 3 H, Me_2bipy), 1.86 (s, 3 H, $COCH_3$). ^{19}F NMR ($CDCl_3$): δ −116.3 (d, 2F$_o$, J(F$_o$F$_m$) = 22.9 Hz), −160.7 (t, 1 F$_p$, J(F$_m$F$_p$) = 20.0 Hz), −162.8 (m, 2 F$_m$). **4**: Yield 60% (Found: C, 51.6; H, 4.0; N, 4.9. $C_{24}H_{23}N_2F_5OPd$ requires C, 51.8; H, 4.2; N, 5.0%); mp 236 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1630, ν(Pd–C_6F_5) 780. ^{1}H NMR ($CDCl_3$) δ: 2.54 (s, 2 H, $PdCH_2$), 2.50 (s, 3 H, Me_2bipy), 2.46 (s, 3 H, Me_2bipy), 2.09 (d, 2 H, CH_2CH, J(HH) = 6.9 Hz), 1.87 (m, 1 H, CH), 0.78 (d, 6 H, CHCH_3, J(HH) = 6.5 Hz). ^{19}F NMR ($CDCl_3$) δ −116.0 (d, 2F$_o$, J(F$_o$F$_m$) = 24.3 Hz), −160.8 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.9 (m, 2 F$_m$). **5**: Yield 69% (Found: C, 49.1; H, 2.8; N, 5.4. $C_{21}H_{13}N_2F_5OPd$ requires C, 49.4; H, 2.6; N, 5.5); mp 250 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1635, ν(Pd–C_6F_5), 780. ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 2 H, $PdCH_2$), 1.95 (s, 3 H, $COCH_3$). ^{19}F NMR ($CDCl_3$): δ −116.0 (d, 2F$_o$, J(F$_o$F$_m$) = 21.4 Hz), −160.4 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.6 (m, 2 F$_m$). **6**: Yield 72% (Found: C, 51.8; H, 3.3; N, 5.3. $C_{24}H_{19}N_2F_5OPd$ requires C, 52.1; H, 3.5; N, 5.1%); mp 244 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1615, ν(Pd–C_6F_5) 790. ^{1}H NMR ($CDCl_3$): δ 2.69 (s, 2 H, $PdCH_2$), 2.14 (d, 2 H, CH_2CH, J(HH) = 7.0 Hz), 1.88 (m, 1 H, CH), 0.77 (d, 6 H, CHCH_3, J(HH) = 6.6 Hz). ^{19}F NMR ($CDCl_3$): δ −116.0 (d, 2F$_o$, J(F$_o$F$_m$) = 23.1 Hz), −160.5 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.8 (m, 2 F$_m$).

Preparation of complexes [Pd(N–N)(C_6F_5){$CH(CO_2Et)_2$}] [N–N = bipy (7) or phen (8)]

To a suspension of the corresponding hydroxo palladium complex [(N–N)Pd(C_6F_5)(OH)] (N–N = bipy or phen) (0.134 mmol) in toluene (15 mL) was added diethylmalonate (24.4 μL, 0.161 mmol). The suspension was boiled under reflux for 7 h to afford a solution from which solvent was partially evaporated under reduced pressure. On addition of hexane the white complexes **7** and **8** precipitated and were filtered off and air-dried. **7**: Yield 71% (Found: C, 46.6; H, 3.0; N 4.7. $C_{23}H_{19}N_2F_5O_4Pd$ requires C, 46.9; H, 3.3; N, 4.8%); mp 187 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1730, ν(Pd–C_6F_5) 790. ^{1}H NMR ($CDCl_3$): δ 3.98 (m, 4 H, CH_2O), 3.52 (s, 1 H, PdCH), 1.12 (t, 6 H, CH_2CH_3, J(HH) = 6.9 Hz). ^{19}F NMR ($CDCl_3$): δ −118.1 (d, 2F$_o$, J(F$_o$F$_m$) = 21.4 Hz), −160.3 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.9 (m, 2 F$_m$). **8**: Yield 69% (Found: C, 49.1; H, 2.9; N 4.7. $C_{25}H_{19}N_2F_5O_4Pd$ requires C 49.0, H 3.1, N 4.6%); mp 228 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1710, ν(Pd–C_6F_5) 790. ^{1}H NMR ($CDCl_3$): δ 3.99 (m, 4 H, CH_2O), 3.65 (s, 1 H, PdCH), 1.13 (t, 6 H, CH_2CH_3, J(HH) = 7.1 Hz). ^{19}F NMR ($CDCl_3$): δ −117.8 (d, 2F$_o$, J(F$_o$F$_m$) = 21.2 Hz), −160.3 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.6 (m, 2 F$_m$).

Preparation of [Pd(tmeda)(C_6F_5){$CH(CO_2Et)_2$}] (9)

To a solution of the hydroxo palladium complex [Pd(tmeda)-(C_6F_5)(OH)] (0.134 mmol) in toluene (15 mL) was added diethylmalonate (24.4 μL, 0.161 mmol). The solution was boiled under reflux for 6 h. The solvent was evaporated-off under reduced pressure. The residue was treated with diethyl ether to render a white solid which was collected by filtration and air-dried. Yield 78% (Found: C, 41.8; H, 4.9; N, 4.8. $C_{19}H_{27}N_2F_5O_4Pd$ requires C, 41.6; H, 5.0; N 5.1%); mp 196 °C (decomp.). IR (Nujol, cm^{-1}): ν(CO) 1685, ν(Pd–C_6F_5) 784. ^{1}H NMR ($CDCl_3$): δ 4.00 (m, 4 H, CH_2O), 2.97 (s, 1 H, PdCH), 2.79 (s, 6 H, CH_3), 2.72 (m, 2 H, CH_2), 2.61 (m, 2 H, CH_2), 2.37 (s, 6 H, CH_3), 1.16 (t, 6 H, CH_2CH_3, J(HH) = 7.1 Hz). ^{19}F NMR ($CDCl_3$): δ −120.7 (d, 2F$_o$, J(F$_o$F$_m$) = 24.5 Hz), −161.0 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −164.2 (m, 2 F$_m$).

Preparation of complexes [Pd(N–N)(C_6F_5){$CH(CN)_2$}] [N–N = bipy (10), phen (11) or tmeda (12)]

To a solution of the corresponding hydroxo palladium complex [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy, phen or tmeda) (0.134 mmol) in methanol (12 mL) was added malononitrile. Spontaneously the white complexes **10** and **11** precipitated. The suspension was stirred for 30 min at room temperature. The white solids were collected by filtration and air-dried. In the case of the more soluble compound **12** the solvent was evaporated-off under reduced pressure. The residue was treated with hexane–ether to render a pale-yellow solid which was collected by filtration and air-dried. **10**: Yield 85% (Found: C, 46.1; H, 2.0; N, 11.1. $C_{19}H_9N_4F_5Pd$ requires C, 46.1; H, 1.8; N, 11.3%); mp 229 °C (decomp.). IR (Nujol, cm^{-1}): ν(CN) 2215, ν(Pd–C_6F_5) 795. ^{1}H NMR ([D$_6$]DMSO): δ 8.70 (m, 3 H), 8.42 (m, 1 H), 8.30 (m, 1 H), 7.96 (m, 1 H), 7.86 (br, 1 H), 7.59 (m, 1 H), 3.54 (s, 1 H, PdCH). ^{19}F NMR ([D$_6$]DMSO): δ −117.5 (d, 2F$_o$, J(F$_o$F$_m$) = 22.9 Hz), −159.7 (t, 1 F$_p$, J(F$_m$F$_p$) = 21.4 Hz), −161.9 (m, 2 F$_m$). **11**: Yield 74% (Found: C, 48.4; H, 1.7; N, 10.6. $C_{21}H_9N_4F_5Pd$ requires C, 48.6; H, 1.8; N, 10.8%); mp 221 °C (decomp.). IR (Nujol, cm^{-1}): ν(CN) 2220, ν(Pd–C_6F_5) 795. ^{1}H NMR ([D$_6$]DMSO): δ 3.71 (s, 1 H, PdCH). ^{19}F NMR ([D$_6$]DMSO): δ −116.8 (d, 2F$_o$, J(F$_o$F$_m$) = 24.3 Hz), −159.7 (t, 1 F$_p$, J(F$_m$F$_p$) = 21.4 Hz), −161.9 (m, 2 F$_m$). **12**: Yield 86% (Found: C, 39.4; H, 4.0; N, 12.0. $C_{15}H_{17}N_4F_5Pd$ requires C, 39.6; H, 3.8; N, 12.3%); mp 187 °C (decomp.). IR (Nujol, cm^{-1}): ν(CN) 2212; ν(Pd–C_6F_5) 788. ^{1}H NMR ($CDCl_3$): δ 2.81 (s, 7 H, CH_3 + PdCH), 2.76 (m, 2 H, CH_2), 2.66 (m, 2 H, CH_2), 2.43 (s, 6 H, CH_3). ^{19}F NMR ($CDCl_3$): δ −119.4 (d, 2F$_o$, J(F$_o$F$_m$) = 21.4 Hz), −158.5 (t, 1 F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −161.5 (m, 2 F$_m$).

Table 5 Crystal structure determination details

	1·½Me_2CO	**9**	**12**	**13**·½CH_2Cl_2
Formula	$C_{19}H_{13}F_5N_2OPd·½Me_2CO$	$C_{19}H_{27}F_5N_2O_4Pd$	$C_{15}H_{17}F_5N_4Pd$	$C_{17}H_{10}ClF_5N_3O_2Pd·½CH_2Cl_2$
M	515.75	548.83	454.73	532.14
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a/Å	8.2813(8)	11.736(3)	11.5401(4)	13.0446(7)
b/Å	8.7515(6)	13.911(5)	8.4604(3)	10.8897(6)
c/Å	13.4037(11)	15.750(6)	17.1175(6)	13.3268(8)
α/°	85.610(6)	104.67(3)	90	90
β/°	78.086(7)	103.00(3)	90.239(1)	109.280(1)
γ/°	84.053(7)	101.02(2)	90	90
V/Å^3	943.86(14)	2338.3(14)	1671.23(10)	1786.92(17)
T/K	293(2)	293(2)	100(2)	100(2)
Z	2	4	4	4
μ/mm^{-1}	1.049	0.859	1.168	1.260
Reflections collected	6641	8209	18592	20422
Independent reflections	3321	8209	3873	4145
R_{int}	0.0195	0.0000	0.0150	0.0279
$R1$ [$I > 2\sigma(I)$][a]	0.0214	0.0399	0.0213	0.0330
wR_2 (all data)[b]	0.0558	0.1041	0.0582	0.0740

[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\, w(F_o2)^2]^{0.5}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Catalytic conversion of malononitrile into its trimer, 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine

[Pd(tmeda)(C_6F_5)(OH)] (30 mg, 0.074 mmol) was added to a solution of malononitrile (487.3 mg, 7. 4 mmol) in wet toluene (20 mL toluene; 2.65 μL H_2O) and the mixture was boiled under reflux for 6 h. The toluene was evaporated under vacuum and the resulting sticky material was treated with ethanol and vigorously stirred to give a beige solid, which was isolated (171 mg, 35% yield), recrystallized from dioxane, dried in the oven at 110 °C and identified as 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine (trimer I). MS: *m*/*z* 198 (M^+, 100%) (Found: C, 54.2; H, 2.9; N, 42.1. $C_9H_6N_6$ requires C, 54.5; H, 3.0; N, 42.4%). IR (Nujol, cm^{-1}): *ν*(NH) 3400–3200, *ν*(CN) 2210. UV-VIS (in MeOH): λ_{max}/nm: 313, 245 (sh), 237. ^{1}H NMR ([D_6]DMSO): *δ* 4.15 (s, 2 H), 7.45 (s, 2 H), 7.65 (s, 2 H).

Preparation of complexes [Pd(N–N)(C_6F_5)(CH_2NO_2)] [N–N = bipy (13) or phen (14)]

A suspension of the corresponding hydroxo palladium complex [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy or phen) (0.134 mmol) in nitromethane (15 mL) was heated for 3–4 h and then concentrated under vacuum until dryness. The residue was extracted in dichloromethane. On addition of hexane the white complexes **13** and **14** precipitated and were filtered off and air-dried. **13**: Yield 74% (Found: C, 41.4; H, 2.3; N, 8.9. $C_{17}H_{10}N_3F_5O_2Pd$ requires C, 41.7; H, 2.1; N, 8.6%); mp 203 °C (decomp.). IR (Nujol, cm^{-1}) *ν*(NO_2) 1560, 1360 cm^{-1}. *ν*(Pd–C_6F_5) 795. ^{1}H NMR ([D_6]DMSO): *δ* 4.69 (s, 2 H, $PdCH_2$). ^{19}F NMR ([D_6]DMSO): *δ* −118.6 (d, 2F_o, *J*(F_oF_m) = 22.9 Hz), −159.8 (t, 1 F_p, *J*(F_mF_p) = 20.0 Hz), −162.4 (m, 2 F_m). **14**: Yield 64% (Found: C, 44.1; H, 2.2; N, 8.4. $C_{19}H_{10}N_3F_5O_2Pd$ requires C, 44.4; H, 2.0; N, 8.2%); mp 263 °C (decomp.). IR (Nujol, cm^{-1}): *ν*(NO_2) 1510, 1360, *ν*(Pd–C_6F_5) 795. ^{1}H NMR ([D_6]DMSO): *δ* 4.92 (s, 2 H, $PdCH_2$). ^{19}F NMR ([D_6]DMSO): *δ* −116.3 (d, 2F_o, *J*(F_oF_m) = 22.9 Hz), −160.4 (t, 1 F_p, *J*(F_mF_p) = 20.0 Hz), −162.6 (m, 2 F_m).

X-Ray crystal structure analysis

Suitable crystals of **1**·½Me_2CO, **9**, **12** and **13**·½CH_2Cl_2 were grown from acetone (complex **1**), toluene–hexane (complex **9**), dichloromethane–toluene–hexane (complex **12**) or from dichloromethane–hexane (complex **13**·½CH_2Cl_2). Mo-Kα radiation was used (*λ* = 0.71073 Å) and the structures were solved by the SHELXS-97[59] program and refined anisotropically on F^2 (program SHELXL-97.[59]) Data collection for **1** and **9** was performed on a Siemens P4 and a Enraf-Nonius CAD 4 diffractometer, respectively, data collection for **12** and **13** was performed on a Bruker Smart CCD diffractometer. Details of data collection and refinement are given in Table 5. The *θ*/° range were 3–25 for **1**, 2–25 for **9** and 2–28 for **12** and **13**. Empirical psi-scan absorption corrections was made in **1** and **9** while SADABS was employed in **12** and **13**.

CCDC reference numbers 243409–243412.

See http://www.rsc.org/suppdata/dt/b4/b409942g/ for crystallographic data in CIF or other electronic format.

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