Stable Palladium–Carbon σ Bonded Complex obtained by Reaction of Acrylonitrile with Palladium Acetate

Maurizio Lenarda,[a] Giorgio Nardin,[b] Giorgio Pellizer,[b] Emile Braye,[c] and Mauro Graziani[b]*

[a] *Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta, Venezia, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Trieste, Piazzale Europa 1, Trieste, Italy*
[c] *ERA, Union Carbide, Bruxelles, Belgium*

Palladium acetate reacts with acrylonitrile to give a 1 : 2 mixture of (*E*)- and (*Z*)-$MeCO_2CH=CHCN$ as the final product; reaction in 1,2-dichloroethane at room temperature gives a stable organopalladium compound, which has been characterised as $Pd(MeCO_2)_2(CH_2=CHCN)$ by *X*-ray crystallography, and represents the first example of an acetoxypalladium intermediate isolated in the absence of stabilizing ligands.

Stable products are usually formed by addition of nucleophiles to palladium co-ordinated dienes,[1] whereas the corresponding adducts from monoalkenes generally decompose during attempted isolation.[2] Reaction of monoalkene palladium complexes with RO^- or $MeCO_2^-$ groups are related to the Wacker process and have been extensively studied. These reactions with palladium co-ordinated alkenes are thought to involve attack by an oxygen nucleophile to produce an alkoxy-(or acetoxy)alkylpalladium intermediate which, to our knowledge has not been isolated in the absence of stabilizing ligands. The compound $(\eta^5\text{-}C_5H_5)Pd(PPh_3)CH_2CH_2OMe$ has been isolated and characterized.[3]

We have studied the reaction of acrylonitrile in the presence of '$Pd(MeCO_2)_2$' which gave as the final product a 1 : 2 mixture

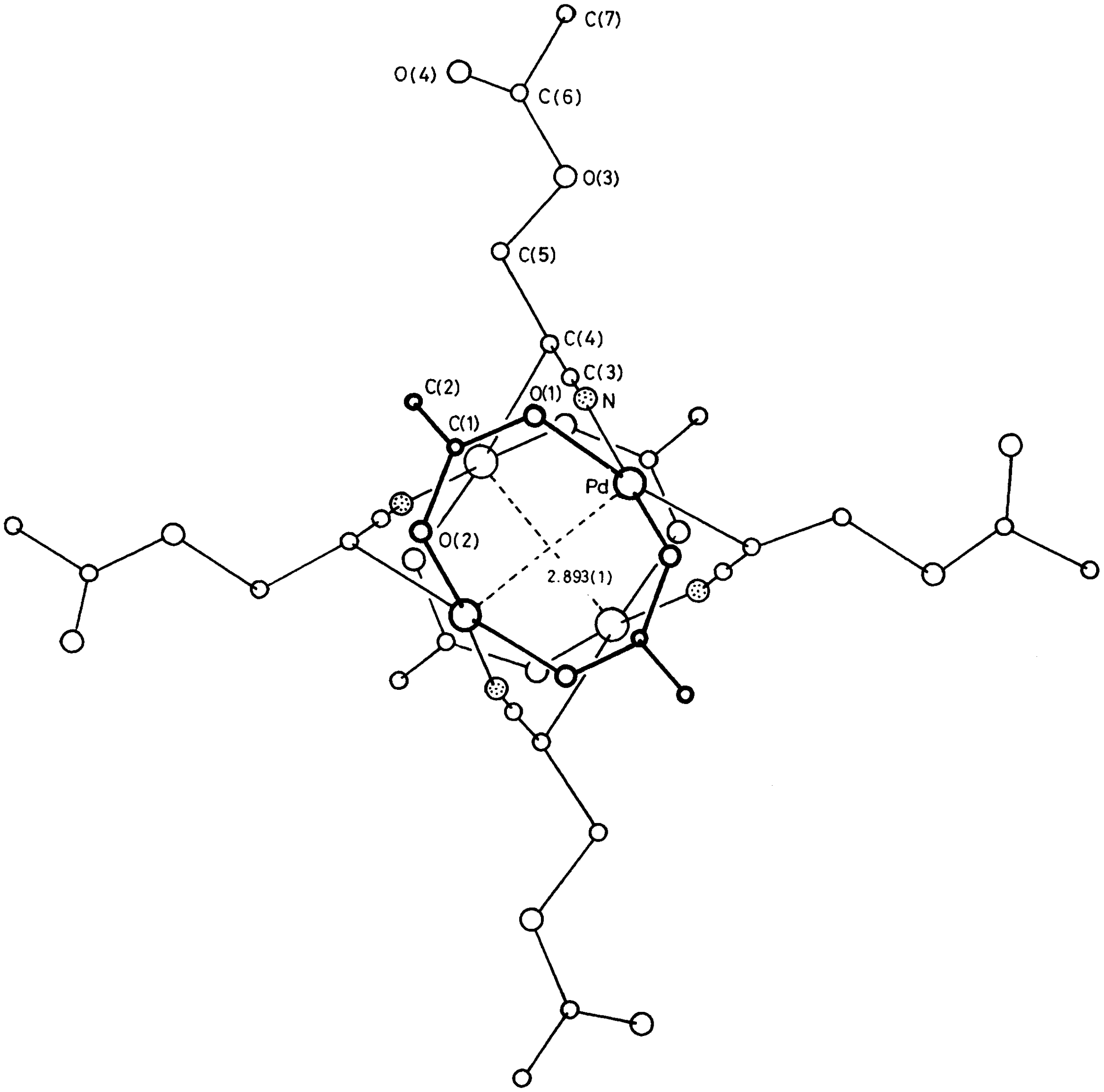

Figure 1. A view of two dimeric units of compound (**1**) along the crystallographic 4_1 axis with the numbering scheme of the independent atoms shown. Pd–Pd distance in Å.

$Pd(MeCO_2)_2(CH_2{=}CHCN)$

(**1**)

of (*E*)- and (*Z*)-cyanovinyl acetate according to reaction (1) and simultaneously afforded palladium metal.[4] However when '$Pd(MeCO_2)_2$' was dissolved in 1,2-dichloroethane and stirred at room temperature for five days in the dark, in the presence of a large excess of $CH_2{=}CHCN$ a red solution was obtained. Separation on silica gel column gave a red-orange product which after crystallization from dioxane was analysed as $Pd(MeCO_2)_2(CH_2{=}CHCN)$ (**1**) by i.r., ^1H, and ^{13}C n.m.r. spectroscopy and *X*-ray diffraction.† Compound (**1**) shows i.r. bands in KBr at 2260m cm^{-1} (ν_{CN}); 1740s, 1220s cm^{-1} (acetate ester); 1580s, 1412m cm^{-1} (acetate anion). The ^1H n.m.r. spectrum, recorded on a VARIAN EM 390 90 MHz spectrometer, exhibits two sharp intense singlets at δ 1.85(3H) and 2.02(3H), attributable to methyl protons of two different acetate groups, together with a doublet of doublets centred at δ 2.85(1H) and a multiplet at δ 4.25(2H) attributed to non-equivalent methylene protons. Much weaker signals are also present in the spectrum probably indicating partial dissociation of the product. The ^{13}C n.m.r. spectrum shows signals at δ 1.2(d, $^1J_{C,H}$ 149 Hz), for methine carbon, at δ 20.7(q, $^1J_{C,H}$ 130 Hz) and 23.5(q, $^1J_{C,H}$ 130 Hz) for methyl carbons, and at δ 62.4(t, $^1J_{C,H}$ 151 Hz) for the methylene carbon. The resonances at δ 131.2, 170.7, and 184.7 are attributed to –CN, ester carbonyl and to the –CO group of the acetate anion, respectively. All these assignments are made by comparison of our data with ^{13}C n.m.r. spectra of related compounds.[5] A strong influence of the metal on the CN carbon atom resonance is observed when compared with the

---

† *Crystal data:* $C_7H_9NO_4Pd \cdot 1$ dioxane (arranged in different sites), tetragonal, space group $I4_1/a$, $a = b = 23.20(4)$, $c = 12.55(5)$ Å, $U = 6757$ Å^3, $D_c = 1.44$ g cm^{-3}, $M = 365.66$, $Z = 16$, μ(Mo-K_α) = 11.0 cm^{-1}, $F(000) = 2944$, $R = 0.061$, $R_w = 0.082$ for 2185 reflections with $I > 3\sigma(I)$ and 3.5° > θ > 27° after absorption correction. The structure was solved by the heavy atom method and refined by full-matrix least squares with hydrogen atoms in calculated positions using computer programs from the CAD4-SDP package.[6] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$-CH_2-CN$ group.[5] All these data are in agreement with the existence of a $(MeCO_2)Pd-CH(CN)CH_2(O_2CMe)$ moiety.

$$CH_2{=}CHCN \xrightarrow{\text{'}Pd(MeCO_2)_2\text{'}} MeCO_2CH{=}CHCN \qquad (1)$$

Single crystals of compound (**1**) were obtained as bright yellow plates and covered with epoxydic cement, as they very rapidly lost crystallinity. The crystal structure of compound (**1**) consists of Pd–Pd units joined by double acetate bridges arranged around the crystallographic 4_1 axis (Figure 1). The cyanoethylacetate moiety acts as a bidentate bridging ligand with two metals of different dimeric units through a palladium–carbon σ bond and nitrile co-ordination. The Pd–Pd distance of 2.893(1) Å can still be regarded as non-binding;[7] the covalent radius of square planar Pd^{II} was estimated as approximately 1.31 Å.[8] The nitrile co-ordination and the acetate bridges probably give the unexpected stability to the complex. Thermal decomposition of compound (**1**) leads, *via* β-extraction, to palladium metal and a 1 : 2 mixture of (*E*)- and (*Z*)-$MeCO_2CH{=}CHCN$ as determined by ^1H n.m.r. spectroscopy.

This work was supported by the University of Trieste and the Ministry of Education (Rome).

Received, 24th May 1985; Com. 713

References

1 J. K. Stille and D. B. Fox, *J. Am. Chem. Soc.*, 1970, **92**, 1274.
2 J. E. Backvall in 'Reactions of Coordinated Ligands,' ed. P. S. Braterman, Plenum Press, New York, 1984.
3 T. Majima and H. Kenosawa, *J. Chem. Soc., Chem. Commun.*, 1977, 610.
4 R. Ros, M. Lenarda, T. Boschi, and R. Roulet, *Inorg. Chim. Acta*, 1977, **25**, 61.
5 J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, London, 1977.
6 B. A. Frenz and Y. Okaya, 'Enraf-Nonius Structure Determination Package,' Enraf-Nonius, Delft, Holland, 1980.
7 M. R. Churchill, H. J. Wasserman, and G. J. Young, *Inorg. Chem.*, 1980, **19**, 762.
8 M. R. Churchill, *Perspect. Struct. Chem.*, 1970, **3**, 91.