# Synthesis of Aldehydes and Ketones through Carbonylation of (9-Methoxytricyclo[5,2,1,$0^{2,6}$]dec-4-en-8-yl)triphenylphosphinepalladium(II) Chloride

By **G. Carturan, M. Graziani,* R. Ros,** and **U. Belluco,** Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Bologna and Facoltà di Chimica Industriale, Università di Venezia, Italy

The complex [Pd($C_{10}H_{12}$OMe)($PPh_3$)Cl] (1) reacts with carbon monoxide in aprotic solvents to give an intermediate which i.r. and n.m.r. spectra indicate to be [Pd{($C_{10}H_{12}$OMe)(CO)}($PPh_3$)(CO)Cl] (2). This intermediate, which could not be isolated, reacts with phenyl- or methyl-lithium to yield unsaturated ketones of the type RCO·$C_{10}H_{12}$·OMe with concomitant reduction of $Pd^{II}$ to metallic palladium. The reaction of (2) with methyl iodide or hydrogen chloride gives the corresponding ketone or aldehyde, respectively, with formation of a palladium(II) dimeric complex. Compound (1) reacts with acetyl chloride to give a $Pd^{II}$ dimeric complex and the ketone MeCO·$C_{10}H_{12}$·OMe which is the same as that obtained by reaction with carbon monoxide and methyl iodide.

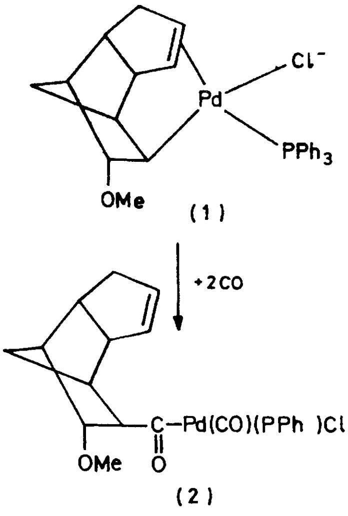
INSERTION of carbon monoxide into palladium–carbon σ bonds is a well known reaction. One of the earliest examples described was the preparation of the acyl derivative [Pd($PEt_3$)$_2$(COMe)Cl] from the corresponding alkyl derivative.[1] Carbon monoxide insertion has been assumed as a step in the synthesis of esters or halides by carbonylation of mono- and di-olefins promoted by palladium salts.[2-7] It is also recognized as a step in the synthesis of diaryl ketones from the reaction of Ar–Hg–Cl (Ar = aryl) in solution with $PdCl_2$ and CO under mild conditions. In this latter case, CO insertion would occur on aryl derivatives of type [Ar–Pd–Cl] prepared *in situ*.[8] The formation of organic carbonyl compounds should occur *via* nucleophilic attack (by $R^-$, $RO^-$, *etc.*) on the acyl group co-ordinated to the metal, formed through CO insertion.

Recently it has been reported that reaction of carbon monoxide under ambient conditions with [Pt($C_{10}H_{12}$OMe)($PPh_3$)Cl], where $C_{10}H_{12}$OMe is 9-methoxytricyclo[5,2,1,$0^{2,6}$]dec-4-en-8-yl, in benzene yields the stable acyl derivative [Pt{($C_{10}H_{12}OCH_3$)(CO)}($PPh_3$)(CO)Cl].[9]

The present paper reports nucleophilic and electrophilic attacks on the analogous acyl palladium(II) derivative prepared *in situ* by carbonylation of the parent alkyl derivative and electrophilic attack by an acyl group on the palladium–carbon σ bond in the alkylpalladium complex.

## RESULTS AND DISCUSSION

The reaction of [Pd($C_{10}H_{12}OCH_3$)($PPh_3$)Cl] (1) with carbon monoxide under mild conditions in solution yields the acyl derivative (2),



which was too unstable to be isolated. It was identified on the basis of two strong bands at 1700 and 1980 cm$^{-1}$ in the i.r. spectrum in $CH_2Cl_2$ solution. These absorptions are assigned to acyl and terminal CO stretching, respectively. If the reaction is carried out in $CDCl_3$

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[1] G. Booth and J. Chatt, *J. Chem. Soc.* (*A*), 1966, 634; *Proc. Chem. Soc.*, 1961, 61.

[2] J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Letters*, 1963, 1437.

[3] S. Brewis and P. R. Hughes, *Chem. Comm.*, 1965, 157; 489.

[4] J. K. Stille and L. F. Hines, *J. Amer. Chem. Soc.*, 1970, **92**, 1798.

[5] M. Graziani, G. Carturan, and U. Belluco, to be published.

[6] J. Tsuji, S. Hosaka, J. Kiji, and T. Susuki, *Bull. Chem. Soc. Japan*, 1966, **39**, 141.

[7] P. M. Henry, *Tetrahedron Letters*, 1968, 2285.

[8] R. F. Heck, *J. Amer. Chem. Soc.*, 1968, **90**, 5546.

[9] G. Carturan, M. Graziani, and U. Belluco, *J. Chem. Soc.* (*A*), 1971, 2509.

the n.m.r. spectrum of the product of the reaction of (1) with CO shows the presence of un-co-ordinated double bond hydrogens at τ 4·5, as expected from a structure of the type shown above. Other n.m.r. features are reported in the Table.

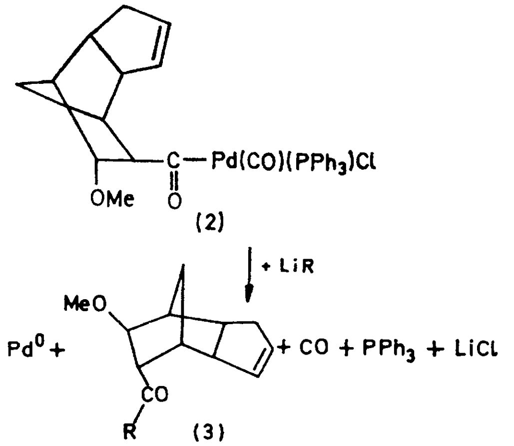
I.r. and n.m.r. spectra of the reaction products of type $MeO{\cdot}C_{10}H_{12}{\cdot}CO{\cdot}R$

| R | τ ($CH_3O$) | τ (R) | $\tau\left(\begin{smallmatrix}-C=C-\\ \mid\ \ \mid\\ H\ \ H\end{smallmatrix}\right)$ | $\nu_{(CO)}$ ($cm^{-1}$) |
|---|---|---|---|---|
| $Pd(PPh_3)(CO)Cl$ | 6·8 | | 4·5 | 1980<br>1700 |
| Me | 6·9 | 7·8 | 4·5 | 1710 |
| Ph | 6·9 | 2·8 | 4·5 | 1720 |
| H | 6·9 | 0·8 | 4·5 | 1730 |

We report below some reactions carried out on the acyl complex (2) and its parent alkyl derivative (1).

*Attack with Nucleophilic and Electrophilic Agents on* $[Pd\{(C_{10}H_{12}OMe)(CO)\}(PPh_3)(CO)Cl]$.— Nucleophilic ($CH_3Li$ and $C_6H_5Li$) and electrophilic agents (MeI and HCl) were allowed to react with (2) prepared *in situ* by the action of CO on $[Pd(C_{10}H_{12}OMe)(PPh_3)Cl]$. In both cases carbon monoxide was removed from the red benzene solution of (2) by purging with nitrogen.

*Nucleophilic Agents.*—The reaction with methyl- and phenyl-lithium in benzene leads to the formation of unsaturated ketone of type (3),

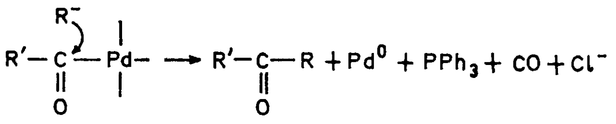


(2)

(3)

with concomitant reduction of $Pd^{II}$ to metallic palladium. The resulting white crystalline ketones were identified by elemental analysis, i.r., and n.m.r. spectra (see Table).

These reactions can be interpreted as nucleophilic attacks of groups $R^-$ ($R^- = Me^-$, $Ph^-$) on the co-ordinated acyl groups:



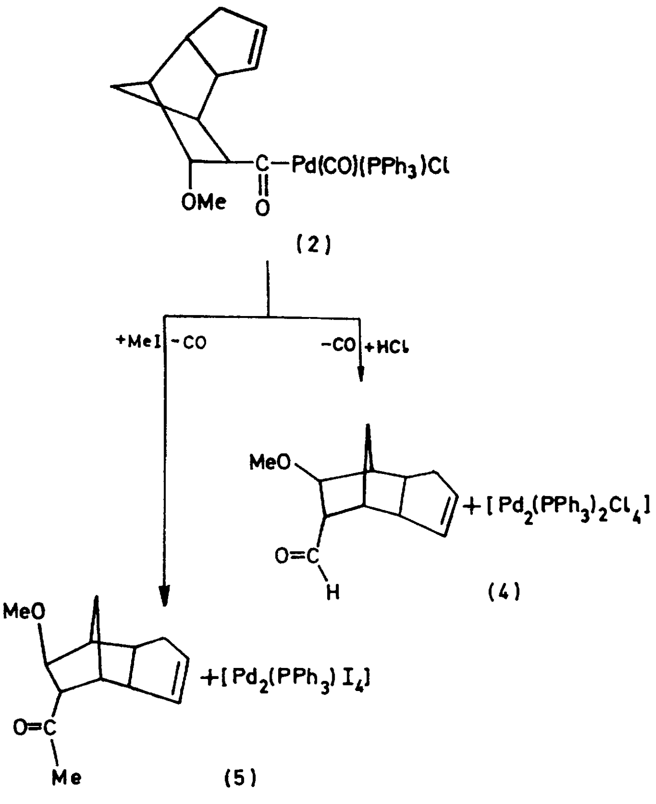
$$R'-\underset{\underset{O}{\|}}{C}\overset{R^-}{\curvearrowleft}-\underset{\mid}{\overset{\mid}{Pd}}- \longrightarrow R'-\underset{\underset{O}{\|}}{C}-R + Pd^0 + PPh_3 + CO + Cl^-$$

( $R' = MeO{\cdot}C_{10}H_{12}$ )

Reduction of the central metal ion upon nucleophilic attack on the co-ordinated organic moiety appears to be a general feature. For example, the carbonylation of ethanol promoted by $PdCl_2$ produces diethyl carbonate and metallic palladium.[10] An analogous reaction involving reduction of co-ordinated metal also takes place in the formation of dialkyl sulphate by nucleophilic attack of $RO^-$ on the $RO_3S^-$ group in $[RO_3S{-}PdCl_2]_2^{2-}$.[11]

*Electrophilic Agents.*—The reactions of (2) with electrophilic agents such as hydrogen chloride and methyl iodide were carried out in benzene at room temperature. At variance with the previous reactions, no reduction to metallic palladium was observed. Instead, an organic carbonyl compound was obtained and palladium was recovered as a dimeric complex of type $[Pd(PPh_3)X_2]_2$ (X = Cl and I, respectively) which was identified by elemental analysis and comparison of the i.r. spectra with that of an authentic sample.[12]

As shown in the Scheme aldehydes or ketones are obtained together with palladium(II) complexes upon reaction with HCl or MeI respectively.



Scheme

The organic product obtained by reaction with methyl iodide was identified by comparison of the i.r. and n.m.r. spectra with an identical compound obtained independently. The aldehyde (obtained in the reaction with HCl) was identified from its i.r. spectrum ($\nu_{CO}$ = 1730 $cm^{-1}$) and n.m.r. spectrum which shows, beside other bands, the characteristic absorptions of the aldehydic

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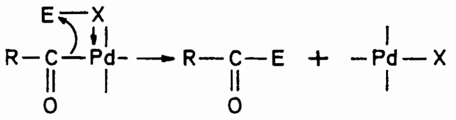
[10] M. Graziani, P. Uguagliati, and G. Carturan, *J. Organometallic Chem.*, 1971, **27**, 275.

[11] M. Graziani, R. Ros, and G. Carturan, *J. Organometallic Chem.*, 1971, **27**, *C*, 19.

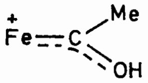
[12] R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1897.

hydrogen at τ 0·8. Both these reactions could be interpreted with a possible reaction path involving an attack of the nucleophilic end, at some stage, on metal and an interaction, not necessarily concerted, of electrons of the acyl–palladium bond with the electrophilic end of the reagent leading to a cyclic transition state:



( R–CO:=MeOC$_{10}$H$_{12}$CO; E–X = H–Cl or MeI )

Without kinetic measurements some other mechanisms could be proposed. It has been reported, for instance, that $(C_5H_5)Fe(CO)(PPh_3)(SO_2CH_3)$[13] and its acyl counterpart $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$[14] can be protonated to give compounds having structure (A). It

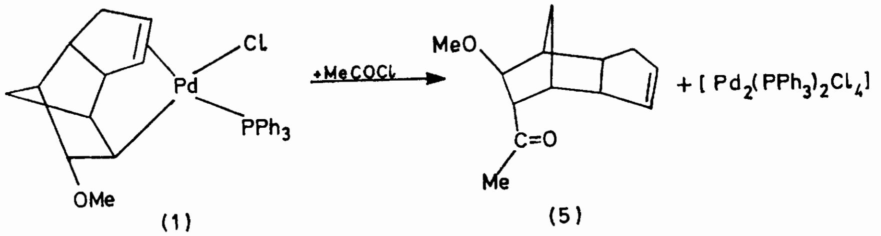


(A)

may well be that similar intermediates could also be present in the reaction of palladium acyl derivatives with HCl.

*Reaction of Electrophilic Agents with* $[Pd(C_{10}H_{12}CH_3O)(PPh_3)Cl]$.—The reaction of (1) with the electrophile acetyl chloride has been examined. This reaction formally corresponds to a stepwise carbonylation of the Pd–C σ bond of (1), followed by attack of the electrophilic end of methyl iodide. The reaction product is identical with that obtained by reaction of methyl iodide on the acyl derivative $[Pd\{(C_{10}H_{12}OCH_3)(CO)\}(PPh_3)(CO)Cl]$.

The resulting ketone was identified by elemental analysis, i.r., and n.m.r. spectra as reported in the Table. The dimeric palladium complex was identified as described above.



(1) (5)

## EXPERIMENTAL

The compound $[Pd(C_{10}H_{12}OMe)(PPh_3)Cl]$ was synthesised as before.[15] Dry benzene was obtained by distillation over Na–K alloy. All other chemicals used were reagent grade materials.

I.r. spectra were recorded on a Perkin-Elmer 621 double-beam spectrophotometer. N.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard, with Varian A 60 or HA 100 instruments.

*Reactions of* $[Pd(C_{10}H_{12}OMe)(PPh_3)Cl]$.—(*a*) *With acetyl chloride.* A dry benzene solution (25 ml) of complex (0·900 g, 1·61 mmol) was stirred under nitrogen with a large excess of acetyl chloride (2 ml, 28 mmol) and the precipitation of the red solid was completed by adding ether. The red material was filtered off and dried *in vacuo*. It was identified by elemental analysis and its i.r. spectrum as $[Pd(PPh_3)Cl_2]_2$.[12] The benzene–ether solution was evaporated under reduced pressure giving an oily product which dissolved in hexane and gave on cooling at −78 °C a white product identified as MeCO·C$_{10}$H$_{12}$·OMe, m.p. 78° ± 1 °C. (Found: C, 75·7; H, 8·4. Calc. for $C_{13}H_{18}O_2$: C, 75·7; H, 8·8%).

(*b*) *With carbon monoxide.* A dry benzene solution (40 ml) of the complex (1·5 g 2·87 mmol) was deaerated by bubbling nitrogen through it for 10 min; it was then stirred at room temperature for two days under carbon monoxide at atmospheric pressure. The solution turned deep red and no precipitation occurred. The reaction was also carried out in $CH_2Cl_2$ and in $CDCl_3$ and the i.r. and n.m.r. spectra of the reaction mixture were recorded. On the basis of its spectra this product was formulated as (2). Attempts to isolate the complex, adding deaerated hexane, gave a dark red material containing Pd, Cl, $PPh_3$, and the methoxide group but, probably because of its great instability, no satisfactory elemental analyses were obtained.

(*c*) *With carbon monoxide followed by phenyl-lithium and methyl-lithium.* The deep red solution containing compound (2), obtained as above was swept with nitrogen to prevent side reactions of CO with LiR.[16] Phenyl-lithium (10 ml, 9·3 mmol) was added dropwise with vigorous stirring under nitrogen. Immediately precipitation of black metallic palladium occurred and the resulting mixture was treated with water to hydrolyse the excess of phenyl-lithium. After filtration to remove metallic palladium, the benzene layer was concentrated and by chromatography on silica gel using hexane–ether as eluant, triphenylphosphine and a colourless oil were obtained. The oil was crystallized by cooling it to give a white solid identified as MeO·C$_{10}$H$_{12}$·COPh, m.p. 43° ± 1 °C (Found: C, 79·8; H, 7·5. Calc. for $C_{18}H_{20}O_2$: C, 80·6; H, 7·51%).

Under the same experimental conditions reaction with methyl-lithium gave the methyl derivative MeO·C$_{10}$H$_{12}$·COMe which was identified by its m.p., elemental analysis and comparison of i.r. and n.m.r. spectra with the product above in reaction (*a*).

(*d*) *With carbon monoxide followed by methyl iodide.* The benzene solution obtained (*b*), after removal of CO with

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[13] M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, 1970, **4**, 347.

[14] M. L. H. Green and C. R. Hurley, *J. Organometallic Chem.*, 1967, **10**, 188.

[15] B. Crociani, P. Uguagliati, T. Boschi, and U. Belluco, *J. Chem. Soc.* (*A*), 1968, 2869.

[16] P. Sutzi and F. W. Schroder, *J. Organometallic Chem.*, 1970, **24**, 1.

nitrogen was refluxed in the dark with methyl iodide (1 ml, 15·9 mmol) for 12 h. The brown solid which precipitated was identified as $[Pd(PPh_3)I_2]_2$ (Found: C, 35·0; H, 2·5; I, 39·7. Calc. for $C_{36}H_{30}I_4P_2Pd_2$: C, 34·7; H, 2·5; I, 40·8%). The filtrate was concentrated to a small volume giving an oily product which was shown to be identical with the organic product obtained in the reaction (*a*) (i.r. and n.m.r.).

(*e*) *With carbon monoxide followed by* HCl. The solution of the complex $[Pd\{(C_{10}H_{12}OMe)(CO)\}(PPh_3)(CO)Cl]$, obtained in (*b*) was treated with anhydrous hydrogen chloride at room temperature for 1 h. The red precipitate was filtered off and dried. It was identified by its i.r. spectrum and elemental analysis as $[Pd(PPh_3)Cl_2]_2$. The resulting colourless solution was evaporated to dryness leaving an oily product whose n.m.r. spectrum in $CDCl_3$ showed a singlet at $\tau$ 0·8 as expected for an aldehydic hydrogen (Found: C, 74·5; H, 8·2. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·9%).

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