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Preliminary communication

THE ACETOXYBROMINATION OF A PALLADIUM(0) COMPLEX

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Summary

$[Pd^0(PhCH{=}CHCOCH{=}CHPh)_2]_n$ reacts with acetyl bromide to give the insoluble $\{Pd^{II}[PhCH{=}CHC(OAc)\cdots CH\cdots CHPh]Br\}_n$; the β-diketonates $\{Pd^{II}[PhCH{=}CHC(OAc)\cdots CH\cdots CHPh](RCOCHCOR)\}$ derived from the bromide exhibit fluxional behaviour between two η^3-allylic forms.

While studies on the structures of the dibenzylideneacetonepalladium(0) complexes, $[Pd(dba)_n]$ [1], and on their reactions with phosphines, olefins and acetylenes [2], have been carried out, little is known of their behaviour in oxidative addition reactions apart from those with allyl chloride to give allylpalladium chloride [1] and with chlorotriphenylmethanes to give η^3-trityl complexes [3]. We report here the reaction with acetyl bromide which proceeds in an unexpected manner.

Reaction of $[Pd(dba)]_2$ with acetyl bromide in chloroform, or with HBr in acetic acid, gave an insoluble brown complex I, $[(C_{19}H_{17}BrO_2Pd)_n]$**, ν(CO) 1753 vs cm^{-1}, in quantitative yield. The insolubility precludes structural studies by NMR, and the complex was therefore converted to the β-diketonates II and III with Tl(RCOCHCOR) (R = Me, CF_3); this reaction was easily reversed on treatment with HBr/HOAc.

With aqueous sodium hydroxide, I regenerated the zerovalent complex $[Pd_2(dba)_3CHCl_3]$ (after crystallisation from $CHCl_3$), together with some metallic palladium. Other reactions are outlined in Scheme 1.

The hexafluoroacetylacetonate complex III, [ν(CO) 1765 vs cm^{-1}] exhibited fluxional behaviour at ambient temperature (^1H NMR ($CDCl_3$ +30 °C) broad weak resonances at δ ca. 5.2 and 7.0 and a broad doublet at 5.97, arising from the vinylic protons) which was frozen out at lower temperatures (at −60°, δ 2.44 (s, CH_3COO), 5.20 and 5.91 [dd, H(1), H(2); J(H(1)—H(2)) 12 Hz], 5.95 (s, hfac CH), 5.97 and 7.09 [dd, H(4), H(5); J(H(4)—H(5)) 15 Hz] and 7.1-7.7 [m, phenyl]).

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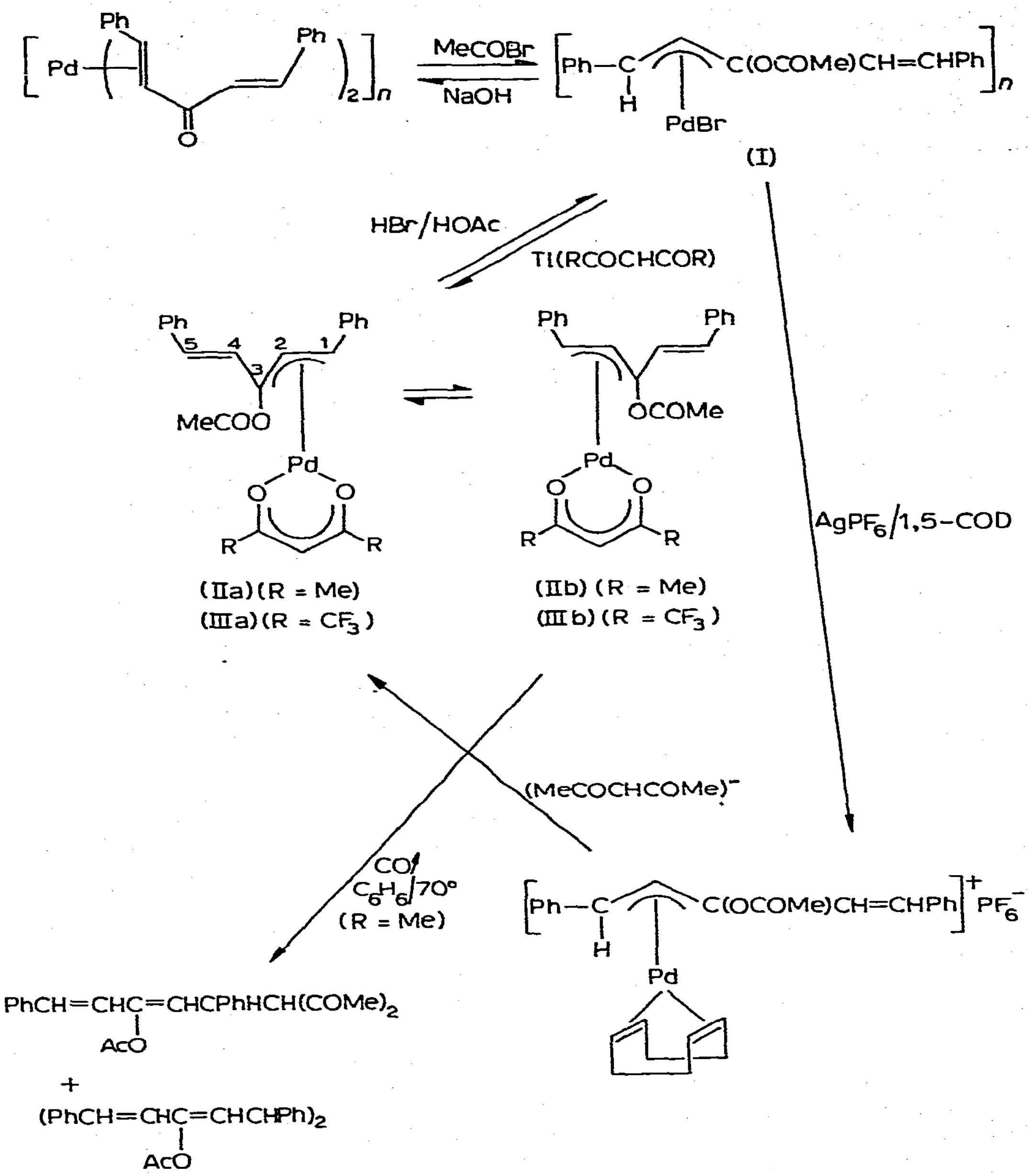
[**] Satisfactory analyses have been obtained for all new compounds.

SCHEME 1



The acetylacetonate II [ν(CO) 1760 vs cm^{-1}] was rigid at +28 °C {^{1}H NMR, δ 1.75, 1.94 (s, acac Me's), 2.31 (s, CH_3COO), 4.90 and 5.74 [dd, H(1), H(2); J(H(1)—H(2)) 12 Hz], 5.20 (s, acac CH), 5.99 and 6.94 [dd, H(4), H(5); J(H(4)—H(5)) 15 Hz], 7.1-7.7 [m, phenyl]}, but these resonances broadened on heating.

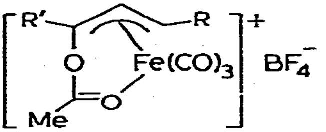
The ^{13}C NMR spectrum of II (in particular, the resonances at δ 75.8, C(1); 98.2, C(2); 101.9, C(3); and 120.1, C(4) or C(5)) is consistent only with allylic bonding (1-3-η) rather than the alternative 1,4,5-η (en-yl). The en-yl form would be expected to show C(3) in the region δ 130-160 and could not account for the signal observed at δ 101.9 [no ^1J(C—H)], while the CH signal due to C(1) (σ-bonded to Pd) would be expected at lower frequency than is actually observed. Similar arguments apply to III.

Line shape analyses [4] of the vinylic protons over the temperature ranges +48 to +101 °C (for II) and +9 to +105 °C (for III) in toluene-d_8 gave activation parameters for the fluxional processes: $\Delta H^{\ddagger} = 62 \pm 6$ (for II), and 55 ± 3 (for III) kJ mol^{-1}, and $\Delta S^{\ddagger} = -44 \pm 17$ (for II) and -37 ± 9 (for III) J K^{-1} mol^{-1}.

The fluxional behaviour arises from dynamic exchanges between two η^3-allylic forms, one where the metal is bonded to C(1), C(2) and C(3), (IIa or IIIa) the other where it bonds to C(3), C(4) and C(5) (IIb or IIIb), and therefore the process is analogous to one described recently for di-μ-chlorobis[4-(chloro-t-butyl)methylene-2,5-di-t-butyl-1-3-η-cyclopent-2-enyl]dipalladium [5]. The stereochemistry at C(3) of the frozen-out form is not known.

The high ν(CO)'s observed for I, II and III indicate that the acetate group is not bonded to the metal. Furthermore, ^{13}C NMR data indicate that C(4)=C(5) does not interact appreciably with the metal in II or III. A possible arrangement of the conformers is as shown.

Nesmeyanov et al. [6] have also recently shown that the complexes [Fe(RCH=CHCR'=O)(CO)$_4$] react with CH$_3$CO$^+$BF$_4$$^-$ to give IV in which the carbonyl also bonds to the metal [ν(CO) ca. 1635 cm^{-1}].



(IV)

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References

1 Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, Chem. Commun., (1970) 1965; K. Moseley and P.M. Maitlis, ibid., (1971) 982; M.C. Mazza and G.G. Pierpont, Inorg. Chem., 12 (1973) 2955; T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, J. Organometal. Chem., 65 (1974) 253.
2 K. Moseley and P.M. Maitlis, J. Chem. Soc. Dalton, (1974) 169; T. Ito, S. Hasegawa, Y. Takahashi, and Y. Ishii, Chem. Commun., (1972) 629.
3 A. Sonoda, B.E. Mann and P.M. Maitlis, Chem. Commun., (1975) 108.
4 I.O. Sutherland, Ann. Rep. N.M.R. Spectroscopy, 4 (1971) 71.
5 P.M. Bailey, B.E. Mann, A. Segnitz, K.L. Kaiser and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1974) 567.
6 A.N. Nesmeyanov, L.V. Rybin, N.T. Gubenko, M.I. Rybinskaya and P.V. Petrovskii, J. Organometal. Chem., 71 (1974) 271.