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Reaction of Pd(η^3-C_3H_5)$_2$ with cyano-olefins; reductive coupling of allyl groups in the presence of triphenylphosphine

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Abstract

Pd(η^3-C_3H_5)$_2$ reacts with tetracyanoethylene (TCNE) to give a 1/1 adduct identified as Pd(η^3-C_3H_5)(η^1-C_3H_5)(TCNE) on the basis of spectroscopic evidence and its behaviour in solution. A similar reaction with fumaronitrile is also described.

The complex Pd(η^3-C_3H_5)(η^1-C_3H_5)(TCNE) reacts with triphenylphosphine to give 1,5-hexadiene and Pd(PPh_3)$_2$(TCNE); a mechanism for this reaction is proposed on the basis of low temperature ^1H and ^{31}P NMR spectroscopy study of the solution during the reaction. The mechanisms are compared with those for the Pt(η^3-C_3H_5) system.

Introduction

Recent trends on the employment of transition metal organometallic compounds as catalysts pay special attention to selectivity features rather than the effectiveness of reactions. This accounts for the growing attention to homoleptic η^3-allylmetal complexes, which behave as catalysts or catalysis intermediates for the formation of a variety of organic molecules [1–4]. The catalytic specificity of these complexes is enhanced by mild working conditions; on the other hand, the nature of metal ion, ligands, solvent, and substrates are important factors which determine the catalytic performance of individual allylic complexes.

We report here the results obtained upon treating Pd(η^3-allyl)$_2$ with TCNE and fumaronitrile in either the presence or absence of phosphine.

The results parallel those for the reactions involving Pt(η^3-allyl)$_2$ [5], which upon treatment with PPh_3 gave the organic product $C_3H_5C_2(CN)_4C_3H_5$.

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Experimental

All chemicals were handled under dry nitrogen. Solvents were dried and purified by standard methods [6], and were degassed by freeze-pump-thaw cycles before each reaction. Pd(η^3-$C_3H_5)_2$ (**1**) was obtained in pentane solution as described elsewhere [1,7]. The concentration of this solution was determined by atomic absorption spectroscopy. The standardized solution was kept in a Schlenk tube in the dark under nitrogen at −20 °C. All other chemicals were obtained from commercial sources and were used as received, except for TCNE, which was sublimed. IR spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer with polystyrene calibration. ^1H NMR spectra were recorded on a Varian Associates FT80A; the reported J values are judged to be accurate within ±0.2 Hz. $^{31}P\ \{^1H\}$ NMR spectra were recorded on a Varian FT80A spectrometer at 32.203 MHz; positive values of chemical shifts are downfield from 85% H_3PO_4, and are judged to be accurate within ±0.1 ppm. Sealed NMR tubes containing weighted amounts of reagents in degassed deuterated solvents were used for analysis.

GC/MS analyses was carried out with a Finningam-MAT 700 Ion Trap Detector mass spectrometer interfaced to a Fractovap series 4160 GC. A bonded-phase fused-silica capillary column (25 m × 0.32 nm; 0V1; 0.10–0.15 μ film) was connected to the "open split" device. The injection port was maintained at 230 °C and the column oven at 30 °C. Samples (1 μl) were injected in a split mode, with split ratio of 1/20. The GC/MS system was controlled by the IBM-XT Personal Computer used either for instrumental control or for mass spectrometric data collection and analysis.

Conductivity measurements were made with a CDM 83 Conductivity Meter.

Preparation of Pd(η^1-C_3H_5)(η^3-C_3H_5)(Y) (Y = TCNE, 2; fumaronitrile, 3)

These compounds were prepared by a standard procedure which is described in detail for complex **2**.

A solution of TCNE (0.175 g; 1.23 mmol) in toluene (ca.15 ml) was added dropwise with stirring to an equimolar amount of Pd(η^3-$C_3H_5)_2$ (**1**) as a 41.1 m*M* pentane solution (30 ml) under nitrogen at −70 °C. After 2 days at −10 °C the yellow solution afforded a yellow precipitate. This was filtered off, washed with pentane, and dried in vacuo. The yield of **2** was 0.325 g (83.5%). Anal. Found: C, 45.0; H, 3.0; N, 17.9. **2**, $PdC_{12}H_{10}N_4$ calcd.: C, 45.50; H, 3.18; N, 17.7%. The yield of **3** was 0.390 g (94%). Anal. Found: C, 44.7; H, 4.4; N, 10.6. **3**, $PdC_{10}H_{12}N_2$ calcd.: C, 45.05; H, 4.50; N, 10.51%.

Reaction of 2 with PPh_3

To a solution of **2** (0.119 g; 0.37 mmol) in CH_2Cl_2 (30 ml) a solution of PPh_3 (0.196 g; 0.75 mmol) in CH_2Cl_2 (30 ml) was added dropwise with stirring at 0 °C. After 8 h at room temperature, a yellow orange solid, **4**, had separated, and this was filtered off, recrystallized from CH_2Cl_2 pentane, and dried in vacuo. The yield of **4** was 0.205 g (71.9%). Anal. Found: C, 66.4; H, 4.0; N, 7.4. **4**, $PdC_{42}H_{30}N_4P_2$ calcd.: C, 66.46; H, 3.98; N, 7.38%. The IR spectrum (Nujol mull) of **4** shows ν(CN) at 2213 and 2175 cm^{-1}. GC/MS analysis of mother liquors showed the presence of 1,5-hexadiene, identified by comparison of its mass spectrum with that of an authentic sample. When the same reaction was carried out in CD_2Cl_2 in a sealed

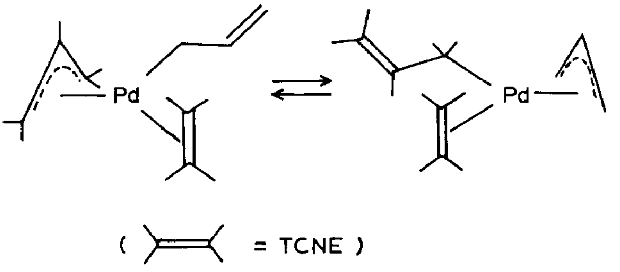
NMR tube, ^{1}H NMR spectroscopy revealed the presence of the signals from 1,5-hexadiene.

Results and discussion

Pd(η^3-allyl)$_2$, which exists as an equilibrium mixture of *trans* and *cis* forms [8], slowly reacts with an equimolar amount of TCNE at $-20\,^\circ$C to give the 1/1 adduct **2** (eq.1).

$$\underset{(\mathbf{1})}{\mathrm{Pd}(\eta^3\text{-}\mathrm{C_3H_5})_2} + \mathrm{TCNE} \rightarrow \underset{(\mathbf{2})}{\mathrm{Pd(C_3H_5)_2(TCNE)}} \qquad (1)$$

The yellow product **2** is fairly stable in air. Its IR spectrum recorded in a Nujol mull shows ν(CN) stretchings at 2259, 2232 and 2184 cm^{-1}; in solution (CH_2Cl_2) there is an absorption at 1603 cm^{-1}, suggesting the presence of a vinyl moiety characteristic of η^1-allyl coordination [9]. Conductivity measurements at 20 °C on ca. 10^{-2} *M* solutions of **2** in 1,2-dichloroethane and acetonitrile give Λ_M values 0.3 and 0.7 Ω^{-1} cm^2 mol^{-1}, respectively, ruling out an ionic structure [10*–12]. The room temperature ^{1}H NMR spectrum of **2** in CD_2Cl_2 solution does not provide any significant evidence for the structure, the signals from the allylic protons appearing as broad multiplets in the range 1–6 ppm. More information is obtained at low temperature ($-76 \pm 2\,^\circ$C). Typical patterns of $CH_2{=}CHCH_2Pd$ protons [13] are observed at (i) 5.47 ppm (1H, central proton as a multiplet), (ii) at 4.88 and 4.96 ppm (two doublets each corresponding to one proton of the terminal CH_2=vinyl group, coupled with the central proton with *J* values of 15 and 9 Hz, respectively), and (iii) 2.02 ppm (2H, methylene protons, CH_2Pd, as a broad doublet coupled by 8 Hz with the central proton). Other signals, integrating in total as five protons, are at 5.77(1H), 3.52(2H), and 1.89–1.32 ppm (2H) as unresolved multiplets. These data do not permit definite assignment of the conformation of allyl groups in **2**. Furthermore, the structure of Pt(η^3-allyl)$_2$(TCNE) with two η^3-allyl groups equivalent, found in the case of Pt(allyl)$_2$ + TCNE reaction, is also ruled out [5]. Indeed, our ^{1}H NMR spectrum at ca. $-76\,^\circ$C parallels that reported for Pd(PMe_3)(η^1,η^3-allyl)$_2$ [1] at temperatures where partial coalescence of allyl protons signals occurs. On this basis, we conclude that allylic moieties in **2** are not equivalent being involved in solution in equilibrium (eq.2) as well as in η^3-allyl conformational equilibria.



(2)

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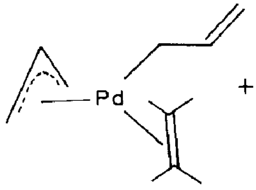
* Reference number with asterisk indicates a note in the list of references.

The same ligand reorganization is suggested also for the Pd(allyl)$_2$(fumaronitrile) adduct, obtained according to eq.3.

$$\underset{(1)}{Pd(\eta^3\text{-}C_3H_5)_2} + NCCH{=}CHCN \rightarrow \underset{(3)}{Pd(C_3H_5)_2(NCCH{=}CHCN)} \qquad (3)$$

Reaction 3 was carried out under the experimental conditions used for **1**. Analytical and conductivity data correspond to the non-ionic species **3**. The IR spectrum of **3** in a Nujoll mull shows the ν(CN) stretching frequency at 2218 cm^{-1}. The ^{1}H NMR results are very similar to those found for **2**. The spectrum at −76 °C in CD_2Cl_2 shows the allylic protons split into two sets of signals, corresponding to η^1-C_3H_5 and η^3-C_3H_5 groups, respectively. For $CH_2{=}CHCH_2Pd$ group the signals are at 5.32 ppm (1H, central proton as a multiplet), 5.03, 4.91 ppm (two doublets each corresponding to one proton of the terminal CH_2=vinyl group, coupled with the central proton by 16 and 8 Hz, respectively), and 2.13 ppm (2H, methylene protons CH_2Pd, as a broad doublet coupled with the central proton by 8 Hz). For the π-bonded allyl group the signals, as unresolved multiplets, appear at 5.36 (1H), 3.58 (2H), and 1.83 ppm (2H). Equilibria of type 2 and dynamic behaviour of the allyl moieties even at −76 °C can account for the equivalence between the fumaronitrile protons, which give a sharp singlet at 6.33 ppm (2H). This may be taken as evidence that the behaviour observed for compounds **2** and **3** in solution in general [14,15].

Reaction of **2** with two equivalents of PPh_3 in CH_2Cl_2 gave a yellow solid and an organic product, with no decomposition to Pd metal. The yellow solid was identified from analytical and spectroscopic data as Pd(PPh$_3$)$_2$(TCNE) (**4**). The ^{31}P {^{1}H} NMR spectrum of **4** in CD_2Cl_2 shows a sharp singlet at 23.5 ppm, as found for an authentic sample [16]. The organic product was identified as 1,5-hexadiene on the basis of the ^{1}H NMR and mass spectral data (eq. 4).



(**2**)

$$+ 2\,PPh_3 \longrightarrow \underset{(\mathbf{4})}{Pd(PPh_3)_2(TCNE)} + 1,5\text{-hexadiene} \qquad (4)$$

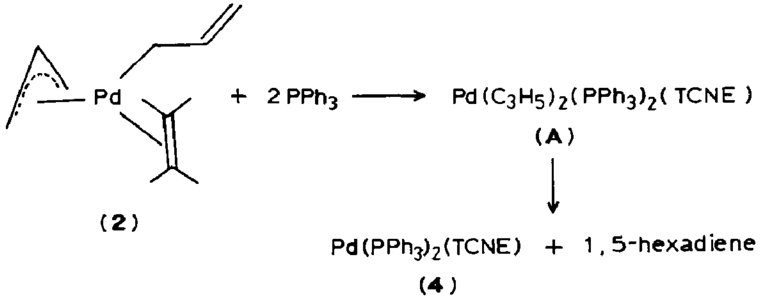
The progress of reaction 4 was studied by ^{1}H and ^{31}P NMR spectroscopy at low temperature in order to elucidate the reaction mechanism. The reaction products obtained in reaction 4 were indeed, found to be different from those formed in the reaction of Pt(allyl)$_2$(TCNE) with PPh$_3$ [5], and the reaction shown in eq. 4 presumably has a substantially different mechanism from that shown in eq. 5.

$$Pt(\eta^3\text{-}C_3H_5)_2(TCNE) \xrightarrow[PPh_3]{} Pt + C_3H_5C_2(CN)_4C_3H_5 \qquad (5)$$

Pt(η^3-allyl)$_2$(TCNE) decomposes in the presence of PPh$_3$ to afford the product of addition of both allyl groups to TCNE (eq. 5). Furthermore, it should be noted that the reductive coupling of allyl groups to yield 1,5-hexadiene may be related to oligomerization and cooligomerization reactions catalyzed by allylmetal complexes [17–20].

The $^{31}P\ \{^1H\}$ NMR spectrum of solution during the reaction recorded at −76 °C 15 min after the mixing of the reagents, showed only two signals, at 32.5 and 23.3 ppm, in ca.1/2 ratio. No signal from free PPh_3 was detected. Since there may be small variations in chemical shifts observed on going from low to room temperature, the signal at 23.3 ppm may be assigned to $Pd(PPh_3)_2(TCNE)$, which gives the signal at 23.5 ppm at room temperature. On the other hand the ^1H NMR spectrum of the same solution, recorded almost simultaneously, showed the presence also of free 1,5-hexadiene, confirming that reaction 4 has already occurred to a significant extent. The ^1H NMR spectrum displayed signals attributable only to η^1-, and not to η^3-allyl groups . The $CH_2{=}CHCH_2Pd$ protons were observed at: 5.49 ppm (1H, central proton as a multiplet), 4.93, 4,87 ppm (two doublets each corresponding to one proton of the terminal vinyl group, $CH_2{=}$, coupled with the central proton by 9 and 17 Hz, respectively), and 1.07 ppm (2H, doublet of doublets coupled by 8 Hz with the central proton and by 9 Hz with phosphorus). As the temperature was raised to 0 °C, about 120 min after the mixing of reagents, the signals from 1,4-hexadiene increased while those of allylic protons decreased.

For comparison, we examined the reaction between $Pd(\eta^3\text{-}C_3H_5)_2$ and two equivalents of PPh_3. At low temperature the $^{31}P\ \{^1H\}$ NMR spectrum displayed the main signal at 33.4 ppm, representing about 90% of total phosphorus present in solution. The corresponding ^1H NMR spectrum showed unresolved broad multiplets with no detectable signals from 1,5-hexadiene. The "$Pd(allyl)_2 + 2PPh_3$" system at room temperature is involved in a slow decomposition reaction giving in addition to 1,5-hexadiene, various unidentified organic products. The reaction of **2** with 2 equivalents of PPh_3 affords only 1,5-hexadiene and $Pd(PPh_3)_2(TCNE)$. These observations enable us to propose the reaction mechanism shown in Scheme 1.



Scheme 1

Intermediate A, with two equivalent $CH_2{=}CHCH_2$ groups and PPh_3 ligands, may be associated with the ^{31}P NMR signal at 32.5 ppm. A trigonal bipyramidal or a square pyramidal conformation is suggested for A, and on the basis of theoretical studies which suggest that a π-coordinating ligand should occupy an equatorial position [21], a trigonal bypiramidal conformation seems more likely.

Scheme 1 does not account for other, possible intermediates for the conversion of A into the final products. The ^1H NMR data obtained in the range −76–0 °C indicate that A is converted into other organometallic species before reductive elimination of 1,5-hexadiene, but the available data do not permit a definite structural formulation of these intermediates. It is of interest that the $PdCH_2CH{=}CH_2$ bonds are not involved in the insertion of TCNE, in contrast to the behaviour of Pt(allyl)$_2$(TCNE) in the presence of phosphine [5]. This fact is attributable to the general features of σ(Pd–C) bonds which permit organic radical coupling much more easily than is the case with platinum(II) analogues [22]. In our system the presence of coordinated TCNE may further enhance the initial reductive elimination of hydrocarbons owing to the good thermodynamic stability of **4**. A recent report by Kurosawa et al. [23] on reductive coupling with allylic palladium(II) complexes is consistent with our results, particularly in respect of the role of electron-withdrawing olefins in promoting reductive elimination.

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