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Cycloaddition of TCNE to *trans*-[(η^1-allyl)Pt(PCy_3)$_2$Cl]

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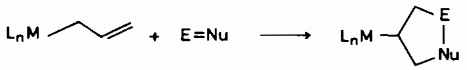
The [3 + 2] cycloaddition reaction between the allylic ligand of 18-electron transition metal-η^1-allyl complexes and various unsaturated substrates leads to the formation of compounds of type *1* (eqn. 1) [1–3].

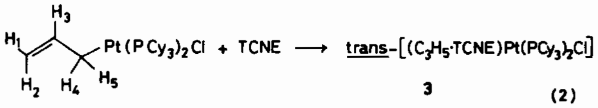


(1)

1

Surprisingly, analogous reactions of coordinatively unsaturated transition metal-η^1-allyl complexes have not been explored. In view of the recent synthesis of square planar platinum(II)-η^1-allyl complexes [4, 5], we endeavored to extend the reaction in eqn. 1 to such 16-electron species. Herein we report the first example of [3 + 2] cycloaddition involving the allylic ligand of a coordinatively unsaturated transition metal complex.

The hitherto unreported starting complex *trans*-[(η^1-C_3H_5)Pt(PCy_3)$_2$Cl], *2*, was obtained as a white solid by reaction of [(C_3H_5)PtCl]$_4$ with PCy_3. This complex was characterized unambiguously as an η^1-allyl derivative by spectroscopic methods (IR in Nujol: $\nu_{C=C}$ 1612 cm^{-1}, ν_{Pt-Cl} 258 cm^{-1}; $^{31}P\{^1H\}$ NMR in C_6H_6: δ 16.90 ppm, J_{Pt-P} 2878 Hz; ^1H NMR in C_6D_6: $\delta(H_1)$ 5.13 ppm, $\delta(H_2)$ 5.40 ppm, $\delta(H_3)$ 6.57 ppm, $H_{4,5}$ masked by PCy_3 protons, $J_{H_1-H_3}$ 9 Hz, $J_{H_2-H_3}$ 17 Hz, $J_{H_3-H_{4,5}}$ 8 Hz). *2* readily reacts in either at 0 °C with a stoichiometric amount of TCNE cleanly to afford product *3* (eqn. 2).



2 3 (2)

The $^{31}P\{^1H\}$ NMR spectrum of *3* (in C_6H_6, δ 15.54 ppm, J_{Pt-P} 2677 Hz) indicates a *trans*-phosphine structure, whereas the IR spectrum (in Nujol, $\nu_{C\equiv N}$ 2256 cm^{-1}, ν_{Pt-Cl} 287 cm^{-1}, no $\nu_{C=C}$) suggests the formation of an adduct between TCNE and the η^1-allyl group of *2*. This is confirmed by the absence of allylic protons in the ^1H NMR spectrum which, owing to the presence of the interfering PCy_3 protons, does not furnish any information concerning the nature of the (C_3H_5·TCNE) moiety. The structure of this fragment was determined by a single-crystal X-ray study of *3*.

Complex *3* crystallized from ether or toluene solutions giving in both cases white needles which degrade at room temperature under X-ray irradiation. From toluene, crystals of *3* were obtained having the monoclinic space group *C2/c* with a = 19.13(2), b = 21.01(2), c = 13.93 Å, β = 108.9(2)°, and Z = 4 formula units. Intensities for 1561 independent reflections having $I > 2\sigma(I)$ collected at ambient temperature using Mo Kα radiation were used in structural determination. These were corrected for Lorentz and polarization factors and for the intensity decrease during data collection apparent in the check reflection values. Anomalous dispersion corrections for Pt, Cl, and P were taken into account. After full-matrix least squares refinement, in which only the Pt, Cl, and P atoms were assigned anisotropic temperature factors, the R value was 0.068. Hydrogen atoms were not included in the calculations. Refinement assuming the non-centrosymmetric space group *Cc* did not improve the results and showed no significant displacement of the atoms from their centrosymmetrically refined positions. Assuming the space group *C2/c* requires the molecule to lie on a crystallographic twofold axis. Since the molecule could possess such a symmetry element only if the CH group bonded to Pt were excluded, we interpret the result in terms of a statistical disorder involving the Pt-bonded carbon around the twofold axis. The crystal decay is consistent with a slight loss of crystal solvent, and in fact the final Fourier maps showed residual broad peaks which could be interpreted as due to a nonstoichiometric amount of weakly bound solvent of crystallization. No attempt was made to locate these poorly resolved solvent atoms.

In spite of the low accuracy of the structural determination owing to poor quality of obtainable crystals, the overall geometry of *3* was unequivocally established. As shown in Fig. 1, the fragment (C_3H_5·TCNE) represents a cyclopentyl ring that resulted from [3 + 2] cycloaddition of TCNE to the η^1-allyl group of *2* with 1,2 Pt metal migration. The structural parameters of the ring are similar within experimental error to those found in [(η^5-C_5H_5)(C_3H_4Me·TCNE)Fe(CO)$_2$] [6], the major difference

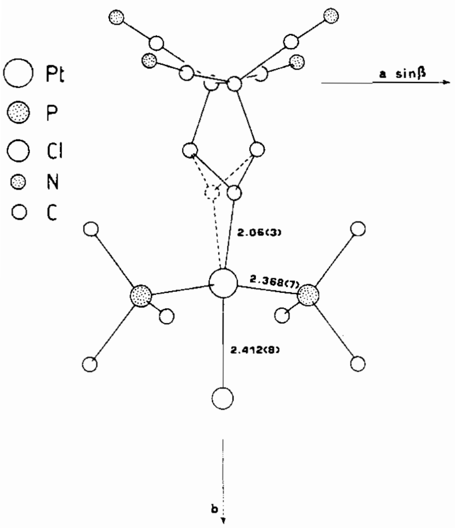


Fig. 1. Stereochemistry of $[(C_3H_5{\cdot}TCNE)Pt(PCy_3)_2Cl]$ as viewed down the *c* axis. For clarity only the α-carbon atoms of the cyclohexyl phosphines are shown. Pt and Cl lie on the crystallographic twofold axis. The two geometries of the disordered cyclopentyl ring are indicated.

being that in the Fe complex the four cyclopentyl carbon atoms not bonded to the metal lie approximately in a plane whereas in the present case there is a torsional angle of −27°.

Thus, the reaction in eqn. 1, originally observed for 18-electron organometallic compounds, extends to 16-electron square planar complexes. This fact suggests the possibility of developing a catalytic route to five-membered organic rings (eqn. 3)

$$C_3H_5X + E{=}Nu \longrightarrow \textit{cyclo-}C_3H_5(X)ENu \qquad (3)$$

by utilizing cycloaddition to coordinatively unsaturated d^8 metal-η^1-allyl complexes and the potential effectiveness of the d^8/d^{10} or d^8/d^6 systems for reductive elimination/oxidative addition reactions. We are currently exploring this synthetic possibility.

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