

Cycloaddition Reactions of Platinum(II)- η^1 -Allyl Complexes with Tetracyanoethylene

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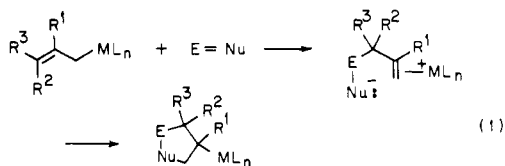
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Received November 18, 1982

Tetracyanoethylene (TCNE) reacts with the 16-electron complexes $[(\eta^1\text{-C}_3\text{H}_5)\text{PtL}_2\text{Cl}]$ (**1a-d**, L = PPh₃, PMePh₂, P-c-Hx₃, or 0.5Ph₂PCH=CHPh₂, respectively) to afford products of [3 + 2] cycloaddition to the allyl fragment $[\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2\text{CHPtL}_2\text{Cl}]$ (**2a-d**). These cycloadducts were characterized by ¹H NMR, ³¹P NMR, and IR spectroscopy; in addition, the structures of the L = P-c-Hx₃ (**2c**) and 0.5Ph₂PCH=CHPh₂ (**2d**) products were determined by single-crystal X-ray diffraction techniques. **2c** crystallizes in the space group C2/c with $a = 19.13$ (2) Å, $b = 21.01$ (2) Å, $c = 13.92$ (2) Å, $\beta = 108.9$ (2)°, $V = 5297$ Å³, and $Z = 4$; **2d** crystallizes in the space group P2₁/c with $a = 8.721$ (8) Å, $b = 16.00$ (1) Å, $c = 26.52$ (2) Å, $\beta = 100.1$ (1)°, $V = 3643$ Å³, and $Z = 4$. Low-temperature ³¹P NMR studies of the reactions of **1a-d** with TCNE in CD₂Cl₂ show that the formation of **2c** and **2d** occurs without any detectable intermediates; by contrast, the formation of each of **2a** and **2b** takes place via two observable species. The results suggest that the cycloaddition proceeds by at least two different mechanisms which depend on the nature of the ligated phosphine. Possible pathways are proposed.

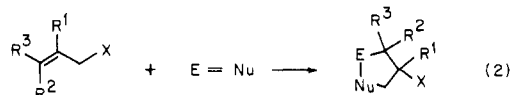
Introduction

Cycloaddition reactions of 18-electron transition-metal- η^1 -allyl complexes with unsaturated electrophilic reagents have been extensively investigated with respect to scope and mechanism.²⁻⁵ They appear to proceed in two steps that involve a dipolar metal- η^2 -olefin intermediate (eq 1, E = electrophilic part, Nu = nucleophilic part).^{6,7}



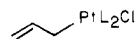
By way of contrast, analogous reactions of 16-electron transition-metal- η^1 -allyl complexes have not been studied. Prompted by the synthesis over the past few years of square-planar platinum(II)- η^1 -allyl complexes,⁸⁻¹⁹ we have

now commenced a study of reactions of such 16-electron species with unsaturated electrophiles, E=Nu. [3 + 2] cycloaddition reactions of coordinatively unsaturated d⁸ complexes have considerable synthetic potential because of the propensity of the d⁸-d¹⁰ and d⁸-d⁶ systems to undergo reductive elimination-oxidative addition processes. These latter reactions would lead to a release of the coordinated five-membered organic ring, thus completing a three-step catalytic cycle for the preparation of cyclic organic compounds from allyl halides and E=Nu (net process, eq 2). 18-Electron cycloadducts are also potential



sources of five-membered organic ring compounds. However, cleavage of the metal-carbon bond therein is generally not a facile process compared to the cleavage in corresponding metal-alkyl complexes.³ When effected under oxidative conditions, it leads to destruction of the organometallic species. Therefore it appears to have only limited applicability to stoichiometric synthesis.

In this paper we describe our initial studies on reactions of the platinum(II)- η^1 -allyl complexes **1** with TCNE. This



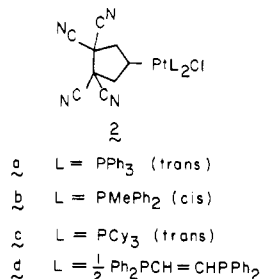
- ↓
- a L = PPh₃ (trans)
 - b L = PMePh₂ (trans)
 - c L = PCy₃ (trans)
 - d L = ½ Ph₂PCH=CHPh₂

electrophile was shown earlier²⁰⁻²³ to be one of the most

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effective reagents for [3 + 2] cycloaddition to the η^1 -allyl fragment of the 18-electron complexes. We now find that TCNE affords analogous [3 + 2] cycloadducts **2** in its reactions with **1**. The products **2c** and **2d** were characterized by single-crystal X-ray diffraction techniques. Some aspects of our investigation on the reaction of **1c** with TCNE, including a summary of the X-ray diffraction results on the product, were communicated earlier in a preliminary form.²⁴



Experimental Section

Materials, Instrumentation, and General Procedures.

Standard techniques were employed for the manipulation of air-sensitive compounds.²⁵ Solvents were dried and distilled under nitrogen. They were degassed by freeze-pump-thaw cycles before use. Commercially obtained phosphines were stored in Schlenk tubes in the dark under nitrogen at -10 °C. TCNE was sublimed before each reaction. [Pt(C₃H₅)Cl]₄ was prepared as reported in the literature.²⁶

IR spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer as Nujol mulls using KBr or CsI windows. The spectra were calibrated with polystyrene; the reported frequencies are accurate to ± 2 cm⁻¹. ¹H NMR spectra were registered on Varian Associates FT 80A and Bruker 270 spectrometers. ³¹P{¹H} NMR measurements were performed on the Varian Associates FT 80A at 32.203 MHz by using either 85% H₃PO₄ as an external standard or CD₂Cl₂ as a field-frequency lock and calibrating the resonance of H₃PO₄ with respect to the signal of the lock.

Preparation of [(η^1 -C₃H₅)PtL₂Cl] (1a-d). These complexes were synthesized by reaction of [Pt(C₃H₅)Cl]₄ in ether suspension with the required amount of phosphine at room temperature under nitrogen for 24 h with magnetic stirring. This known procedure^{16,17} leads to the isolation of white products in virtually quantitative yield. The previously reported **1a** (L = PPh₃) and **1c** (L = P-c-Hx₃) were characterized by comparison of their spectroscopic properties with those given in the literature.^{14,16,17,24,26} Anal. Calcd for **1b** (L = PMePh₂), PtC₂₅H₃₁ClP₂: C, 51.82; H, 4.65; Cl, 5.27. Found: C, 51.4; H, 4.9; Cl, 5.1. Anal. Calcd for **1d** (L = 0.5Ph₂PCH=CHPPh₂), PtC₂₅H₂₇ClP₂: C, 52.14; H, 4.07; Cl, 5.31. Found: C, 53.1; H, 3.9; Cl, 5.2.

Preparation of [(η^1 -C₃H₅)PtL₂]⁺BF₄⁻ (L = PPh₃, PMePh₂, P-c-Hx₃, and 0.5Ph₂PCH=CHPPh₂). These products were prepared by treatment of the corresponding complex **1** with AgBF₄ in CH₂Cl₂ solution under nitrogen with stirring. The precipitated AgCl was filtered off, and the filtrate was concentrated to a small volume. Addition of ether induced the precipitation of the title product. The known PPh₃, PMePh₂, and P-c-Hx₃ complexes were identified by comparison of their ¹H and ³¹P NMR spectra with those reported in the literature.^{14,16-19,27-30} Anal. Calcd for the L = 0.5Ph₂PCH=CHPPh₂ complex, PtC₂₅H₂₇BF₄P₂: C, 48.41; H, 3.74. Found: C, 47.4; H, 3.9.

Reaction of [(η^1 -C₃H₅)PtL₂Cl] (1a-d) with TCNE. (a) **1d** (L = 0.5Ph₂PCH=CHPPh₂). A solid mixture of **1d** (0.841 g,

1.26 mmol) and TCNE (0.161 g, 1.26 mmol) under nitrogen was treated with 40 mL of dry toluene at -78 °C. The contents were stirred at -70 to -80 °C for 3 days, and then a pale yellow crystalline solid was filtered off at low temperature, washed with ether, and dried in vacuo. The yield of **2d** was 0.699 g (64%): IR $\nu_{\text{Pt-Cl}}$ 324, $\nu_{\text{C=N}}$ 2184 (m), 2236 (w) cm⁻¹. Anal. Calcd for PtC₃₃H₂₇ClN₄P₂: C, 52.80; H, 3.42; N, 7.03. Found: C, 53.1; H, 3.3; N, 6.9.

(b) **1a** (L = PPh₃). With use of a procedure analogous to that described above, 0.511 g (70% yield) of product, **2a**, was obtained by reaction of 0.622 g of **1a** with 1 equiv of TCNE (0.100 g, 0.784 mmol): IR $\nu_{\text{Pt-Cl}}$ 310, $\nu_{\text{C=N}}$ 2110 (m), 2200 (vw), 2260 (w) cm⁻¹. Anal. Calcd for PtC₄₅H₃₅ClN₄P₂: C, 58.47; H, 3.82; N, 6.06. Found: C, 59.1; H, 3.8; N, 5.8.

(c) **1b** (L = PMePh₂). Similarly, reaction of **1b** (0.754 g) with an equivalent amount of TCNE (0.144 g, 1.12 mmol) afforded 0.490 g (54% yield) of product **2b**: IR $\nu_{\text{Pt-Cl}}$ 303, $\nu_{\text{C=N}}$ 2192 (m), 2223 (w) cm⁻¹. Anal. Calcd for PtC₃₅H₃₁ClN₄P₂: C, 52.53; H, 3.81; N, 7.00. Found: C, 53.0; H, 3.8; N, 6.8.

(d) **1c** (L = P-c-Hx₃). The corresponding 1:1 adduct **2c** was prepared as described earlier.²⁴

Crystal Data and Structure Determinations. **2c**: PtC₄₅H₃₅ClN₄P₂, fw 960.7, monoclinic, *a* = 19.13 (2) Å, *b* = 21.01 (2) Å, *c* = 13.92 (2) Å, β = 108.9 (2)°, *V* = 5297 Å³, *Z* = 4, *D*_{calcd} = 1.20 g cm⁻³, Mo K α radiation, λ = 0.7107 Å, μ (Mo K α) = 29.3 cm⁻¹, space group *C2/c*.

2d: PtC₃₅H₂₇ClN₄P₂, fw 796.2, monoclinic, *a* = 8.721 (8) Å, *b* = 16.00 (1) Å, *c* = 26.52 (2) Å, β = 100.1 (1)°, *V* = 3643 Å³, *Z* = 4, *D*_{calcd} = 1.45 g cm⁻³, Mo K α radiation, λ = 0.7107 Å, μ (Mo K α) = 42.4 cm⁻¹, space group *P2₁/c*.

Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line automated single-crystal diffractometer.

Three-dimensional intensity data were collected at room temperature on the Siemens diffractometer by the θ - 2θ scan technique with Mo K α radiation for a maximum 2θ angle of 50° for both compounds. Reflections with *I* < 2 θ (*I*) for **2c** and *I* < 3 σ (*I*) for **2d** were rejected, and the remaining reflections were corrected for the Lorentz and polarization factors. Correction was also made for **2c** taking into account the intensity decrease of the reference reflection observed during data collection. A total of 1561 independent reflections for **2c** and 2455 for **2d** were used in the subsequent calculations. Corrections for the real and imaginary parts of the anomalous dispersion was applied to Pt, Cl, and P.³¹ No correction for absorption was made in view of the small size of crystals.

Both structures were solved by conventional Patterson and Fourier methods. After least-squares refinement (full matrix for **2c** and block-diagonal matrix for **2d**), in which only the Pt, Cl, and P atoms were assigned anisotropic temperature factors, the *R* value was 0.068 (*R*_w = 0.098) for **2c** and 0.043 (*R*_w = 0.058) for **2d**. Hydrogen atoms were included only in the calculations of **2d**, their contribution being held constant (*B* = 7.0 Å²) during refinement. Refinement of **2c** in the noncentrosymmetric space group *Cc* did not improve the results and showed no significant displacement of the atoms from their centrosymmetrically refined positions. On the other hand, 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 results in terms of a statistical disorder involving the Pt-bonded carbon atom around the twofold axis.

The crystal decay of **2c** suggests a slight loss of crystal solvent, which is consistent with the final Fourier map showing residual broad peaks attributable to a nonstoichiometric amount of weakly bound solvent of crystallization. No attempt was made to locate these poorly resolved solvent atoms.

Final atomic parameters are listed in Tables I and II together with their estimated standard deviations calculated from the inverse matrix of the final least-squares cycle. A listing of structure factors is available as supplementary material.³²

Calculations were carried out by using local programs and X-ray

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Table I. Fractional Coordinates ($\times 10^4$) and Temperature Factors (\AA^2) of 2c, with Estimated Standard Deviations in Parentheses^a

	x	y	z	B		x	y	z	B
Pt	0 (0)	2114 (1)	2500 (0)		C(10)	2074 (17)	3507 (14)	4129 (25)	7.9 (8)
Cl	0 (0)	3262 (4)	2500 (0)		C(11)	1781 (13)	2831 (12)	3668 (20)	5.6 (5)
P	991 (3)	2214 (3)	1842 (5)		C(12)	1601 (13)	1492 (11)	1826 (20)	5.1 (5)
N(1)	1301 (17)	-746 (14)	3722 (24)	9.5 (8)	C(13)	2062 (16)	1531 (13)	1127 (24)	7.0 (7)
N(2)	-827 (15)	-203 (12)	3992 (21)	8.3 (6)	C(14)	2489 (19)	873 (16)	1139 (28)	8.9 (9)
C(1)	-170 (21)	1149 (15)	2588 (38)	2.6 (9)	C(15)	2965 (19)	730 (16)	2260 (27)	8.6 (9)
C(2)	465 (15)	770 (12)	3380 (22)	5.8 (6)	C(16)	2500 (17)	713 (13)	2958 (24)	7.0 (7)
C(3)	176 (14)	39 (12)	3175 (19)	5.4 (6)	C(17)	2101 (14)	1357 (13)	2944 (22)	6.4 (6)
C(4)	813 (18)	-408 (15)	3493 (25)	7.7 (7)	C(18)	654 (12)	2440 (10)	459 (18)	4.3 (5)
C(5)	-397 (15)	-125 (12)	3637 (20)	5.3 (6)	C(19)	256 (5)	3092 (12)	282 (21)	6.3 (6)
C(6)	1590 (12)	2906 (12)	2472 (18)	4.8 (5)	C(20)	-2 (16)	3230 (14)	-937 (23)	6.8 (7)
C(7)	2266 (17)	3060 (14)	2106 (24)	7.6 (7)	C(21)	-540 (16)	2711 (13)	-1445 (23)	6.9 (7)
C(8)	2603 (20)	3721 (19)	2619 (30)	9.8 (9)	C(22)	-184 (15)	2012 (14)	-1286 (22)	6.9 (7)
C(9)	2762 (18)	3707 (17)	3813 (27)	8.8 (8)	C(23)	85 (14)	1909 (11)	-87 (20)	5.6 (6)
	B_{11}	B_{12}	B_{13}		B_{22}	B_{23}	B_{33}		
Pt	4.92 (6)	0.00 (0)	0.34 (4)		2.59 (5)	0.00 (0)	3.02 (7)		
Cl	6.62 (52)	0.00 (0)	2.46 (44)		2.84 (35)	0.00 (0)	6.68 (59)		
P	4.71 (27)	0.21 (22)	0.19 (23)		3.92 (29)	-0.20 (23)	4.40 (35)		

^a Anisotropic temperature factors are in the form $\exp(-[h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23}])$.

Table II. Fractional Coordinates ($\times 10^4$) and Temperature Factors (\AA^2) of 2d, with Estimated Standard Deviations in Parentheses^a

	x	y	z	B		x	y	z	B
Pt	3081 (1)	281 (0)	1996 (0)		C(28)	-1416 (26)	2407 (14)	1168 (8)	6.3 (5)
P(1)	4796 (5)	745 (3)	2693 (2)		C(29)	155 (21)	2183 (12)	1181 (7)	4.7 (4)
P(2)	2996 (5)	1570 (3)	1721 (2)		C(30)	3672 (19)	1801 (10)	1125 (6)	3.9 (3)
Cl	3029 (6)	-1101 (3)	2305 (2)		C(31)	3657 (21)	2602 (11)	938 (7)	4.9 (4)
N(1)	-3776 (26)	-1216 (14)	1186 (8)	9.2 (6)	C(32)	4172 (25)	2773 (14)	473 (8)	6.2 (5)
N(2)	-1713 (23)	286 (13)	192 (7)	7.8 (4)	C(33)	4726 (25)	2145 (14)	215 (8)	6.3 (5)
N(3)	-477 (26)	-2059 (14)	76 (8)	9.0 (6)	C(34)	4803 (25)	1348 (14)	386 (8)	6.3 (5)
N(4)	-101 (24)	-2509 (13)	1627 (8)	8.2 (5)	C(35)	4229 (22)	1144 (11)	864 (7)	5.0 (4)
C(1)	1410 (20)	-39 (10)	1339 (7)	4.2 (4)	H(1)	1382	428	1070	7.0
C(2)	-196 (20)	-125 (11)	1488 (6)	4.5 (4)	1-H(2)	-96	-421	1827	7.0
C(3)	-1146 (22)	-657 (12)	1039 (7)	5.2 (4)	2-H(2)	-687	434	1517	7.0
C(4)	63 (21)	-1341 (11)	960 (7)	4.5 (4)	1-H(5)	2158	-820	755	7.0
C(5)	1717 (21)	-888 (12)	1082 (7)	4.6 (4)	2-H(5)	2477	-1252	1322	7.0
C(6)	-2612 (24)	-977 (13)	1116 (8)	5.8 (5)	H(10)	5767	2183	2860	7.0
C(7)	-1458 (23)	-128 (13)	552 (8)	5.8 (4)	H(11)	4303	2837	2124	7.0
C(8)	-244 (24)	-1730 (13)	464 (8)	5.8 (5)	H(13)	7697	1188	3323	7.0
C(9)	21 (25)	-2003 (14)	1340 (8)	6.4 (5)	H(14)	410	658	3385	7.0
C(10)	5053 (19)	1856 (10)	2608 (6)	3.8 (3)	H(15)	772	-714	3059	7.0
C(11)	4223 (19)	2219 (10)	2184 (6)	3.8 (3)	H(16)	8704	-1326	2448	7.0
C(12)	6747 (18)	298 (11)	2799 (6)	4.0 (3)	H(17)	6120	-719	2322	7.0
C(13)	7937 (28)	676 (15)	3120 (9)	7.1 (5)	H(19)	3755	1943	3407	7.0
C(14)	9501 (29)	338 (16)	3193 (9)	7.8 (6)	H(20)	2974	1783	4229	7.0
C(15)	9731 (27)	-416 (14)	2973 (8)	6.9 (5)	H(21)	2895	483	4585	7.0
C(16)	8495 (24)	-800 (14)	2643 (8)	5.9 (5)	H(22)	3520	-739	4166	7.0
C(17)	7000 (23)	-425 (12)	2551 (7)	5.5 (4)	H(23)	4459	-600	3371	7.0
C(18)	4195 (19)	687 (10)	3319 (6)	3.8 (3)	H(25)	1034	1953	2428	7.0
C(19)	3749 (23)	1367 (13)	3566 (8)	5.6 (4)	H(26)	-1051	2314	2379	7.0
C(20)	3257 (26)	1290 (14)	4042 (8)	6.5 (5)	H(27)	-3153	2622	1570	7.0
C(21)	3219 (25)	531 (13)	4245 (8)	6.1 (5)	H(28)	-2076	2530	833	7.0
C(22)	3631 (25)	-172 (14)	4008 (8)	6.5 (5)	H(29)	658	2170	867	7.0
C(23)	4149 (23)	-89 (13)	3544 (8)	5.7 (4)	H(31)	3264	3082	1131	7.0
C(24)	1020 (17)	1992 (9)	1654 (6)	3.1 (3)	H(32)	4171	3342	325	7.0
C(25)	368 (19)	2043 (10)	2089 (6)	4.0 (3)	H(33)	5112	2264	-118	7.0
C(26)	-1146 (24)	2285 (13)	2064 (7)	5.5 (4)	H(34)	5228	881	182	7.0
C(27)	-2020 (24)	2463 (13)	1594 (8)	5.6 (4)	H(35)	4268	564	996	7.0
	B_{11}	B_{12}	B_{13}		B_{22}	B_{23}	B_{33}		
Pt	3.22 (4)	-0.05 (4)	0.13 (2)		2.75 (4)	-0.09 (3)	2.77 (4)		
P(1)	3.60 (21)	0.20 (17)	0.06 (15)		3.69 (19)	0.15 (16)	3.15 (18)		
P(2)	3.10 (19)	-0.06 (16)	0.28 (15)		3.09 (17)	-0.14 (15)	3.44 (18)		
Cl	5.26 (14)	-0.18 (18)	0.10 (18)		3.53 (19)	-0.54 (17)	5.25 (23)		

^a Anisotropic temperature factors are in the form $\exp(-[h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23}])$.

70 system.³³ Atomic scattering factors were calculated as reported.³⁴

Results and Discussion

Preparation and Spectroscopic Characterization of Cycloaddition Complexes. The precursor platinum-

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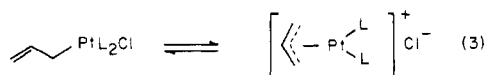
Table III. ^{31}P NMR Data^a for Metal-Allyl Species Present in CD_2Cl_2 (CH_2Cl_2) Solution at ca. -69°C

starting complex	complex(es) in soln	%	δ	$J_{^{195}\text{Pt}-\text{P}}$, Hz
1a	$[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}(\text{PPh}_3)_2]^+\text{Cl}^-$ ^b	100	15.5	3940
1b	$[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}(\text{PMePh}_2)_2]^+\text{Cl}^-$ ^c	100	-0.2	3868
1c	1c ^d	40	16.9	2878
	$[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}(\text{PCy}_3)_2]^+\text{Cl}^-$ ^e	60	28.4	3802
			27.7	3706
1d	1d	70	54.8	1836
			53.1	4347
	$[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}(\text{Ph}_2\text{PCH=CHPh}_2)]^+\text{Cl}^-$ ^c	30	58.1	3718

^a δ values ± 0.1 ppm, J values ± 4 Hz. ^b Also quoted in ref 14, 16, 17, and 19. ^c Assigned by comparison with the spectrum of the corresponding $[(\eta^3\text{-C}_3\text{H}_5)_2\text{PtL}_2]^+\text{BF}_4^-$. ^d Data in C_6H_6 solution reported in ref 24. ^e An AB spectrum; see ref 29.

(II)- η^1 -allyl complexes **1a-d** were characterized on the basis of elemental analysis and spectroscopic properties. In the IR spectra, the absorption at $1625\text{--}1610\text{ cm}^{-2}$ has been assigned to $\nu_{\text{C}=\text{C}}$ of the free olefinic end of C_3H_5 , and a $\nu_{\text{Pt}-\text{Cl}}$ in the range $280\text{--}260\text{ cm}^{-1}$ indicates that Cl^- is trans to $\eta^1\text{-C}_3\text{H}_5$ for **1a-c**. Low solubilities of these complexes in nonpolar solvents hampered in some cases identification by NMR spectroscopy. On the other hand, use of polar solvents such as CH_2Cl_2 or CHCl_3 leads to the establishment of rapid equilibria involving **1**, $[(\eta^3\text{-C}_3\text{H}_5)_2\text{PtLCl}]$ and **L**, and, especially, $[(\eta^3\text{-C}_3\text{H}_5)_2\text{PtL}_2]^+\text{Cl}^-$.^{15-19,28} Accordingly, the ^{31}P NMR spectra in CH_2Cl_2 (CD_2Cl_2) at 26°C show a broad signal with no detectable satellites expected from $^{195}\text{Pt}\text{-}^{31}\text{P}$ coupling. However, at temperatures of -50 to -80°C , the signal sharpens and the spectra allow the identification of the species present in solution. The assignments presented in Table III have been made on the basis of the magnitude of $J_{^{195}\text{Pt}-\text{P}}$, which is a very sensitive tool for the characterization of platinum(II)-phosphine complexes.^{19,35-37} The relative amounts of the species present were determined by measuring the height of the corresponding ^{31}P NMR peaks. A gradual decomposition of these complexes in CH_2Cl_2 solution, which occurs at ambient temperatures, appears to be arrested at ca. -69°C .

The ^{31}P NMR data in Table III confirm the presence of the equilibrium (eq 3) for **1c** and **1d** and show $[(\eta^3\text{-C}_3\text{H}_5)_2\text{PtL}_2]^+\text{Cl}^-$ as the only observable species when $\text{L} = \text{PPh}_3$ and PMePh_2 . Because of the predominance of



$[(\eta^3\text{-C}_3\text{H}_5)_2\text{PtL}_2]^+\text{Cl}^-$ in CH_2Cl_2 solution, reactions between **1** and TCNE were conducted in the less polar solvent ether or toluene, where the relative concentration of the η^1 -allyl complex is higher.

The synthesis of **2c** can be effected in good yield from **1c** and TCNE in ether or toluene at 0°C . In contrast, dropwise addition of a TCNE solution to each of **1a**, **1b**, and **1d** in CH_2Cl_2 solution or in toluene suspension at 0°C immediately causes the appearance of blue color. The yellow-green precipitates obtained by dilution with hexane do not analyze as 1:1 adducts of the reactants and appear to be mixtures. However, when the foregoing reactions are conducted as a slurry in toluene at -70 to -80°C , 1:1 adducts result. Elemental analysis suggests that these products contain solvent of crystallization.

The ^1H and ^{31}P NMR data for the new cycloaddition complexes **2** are set out in Table IV. The spectra were recorded in CD_2Cl_2 solution, in which these products are quite soluble and stable.

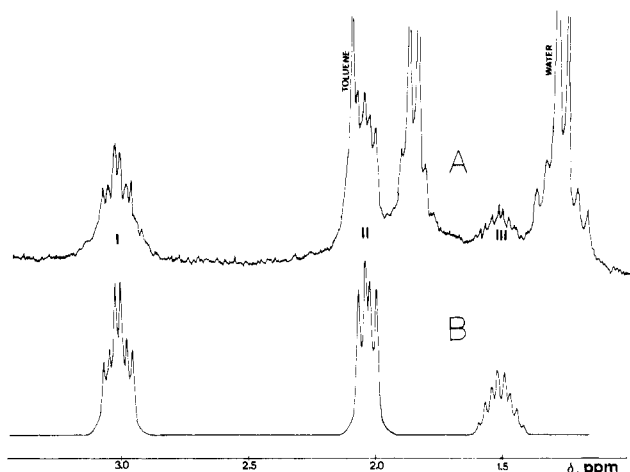
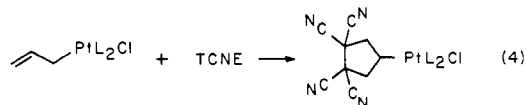


Figure 1. ^1H NMR spectrum of **2b** in the region δ 3.5-1.0: (A) experimental, in CD_2Cl_2 at 26°C ; (B) simulated, cyclopentyl protons only, without inclusion of possible coupling with ^{195}Pt .

The ^{31}P NMR spectra reveal the symmetry of the square-planar coordination environment of platinum(II). The complexes **1a** and **1c** react with TCNE with retention of the trans geometry, as indicated by one ^{31}P signal and a $J_{^{195}\text{Pt}-\text{P}}$ in the range $2650\text{--}3010$ Hz in the spectra of the products **2a** and **2c**, respectively. In contrast, **1b** and TCNE afford a cis cycloadduct, **2b**. The ^{31}P NMR spectra of **2b** and of the product derived from **1d** and TCNE, **2d**, each show two ^{31}P signals, which are doublets with appropriate ^{195}Pt satellites. The lower field resonances are characterized by $J_{^{195}\text{Pt}-\text{P}}$ values of 1905 and 1951 Hz, respectively, which suggest the presence of a $(\text{C}_3\text{H}_5\text{,TCNE})$ group σ bonded through carbon to platinum in the position trans to phosphorus. These data and the absence of $\nu_{\text{C}=\text{C}}$ in the IR spectra of products point to the formation of [3 + 2] cycloaddition complexes (eq 4). This inference was



corroborated by the determination of the molecular structures of the cycloadducts **2c** and **2d** by single-crystal X-ray diffraction techniques (vide infra). Since all four products show similar features in their ^1H NMR spectra, there is little doubt that they all contain the same five-

membered cyclic ligand $\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$. The observed change of geometry on going from **1b** (trans) to **2b** (cis) may be caused by the reacting TCNE or another ligating species. It is well recognized^{38,39} that isomerization

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Table IV. ^{31}P and ^1H NMR Data for Cycloaddition Complexes, **2**, in CD_2Cl_2 Solution

complex	^{31}P NMR			^1H NMR, ^c δ^d and J^e			
	δ^a	$J_{^{195}\text{Pt}-\text{P}}^b$	$J_{\text{P}-\text{P}}$	$\text{H}_{\text{A,A}'}$	$\text{H}_{\text{B,B}'}$	H_{C}	phosphine H's
2a	25.2	3007	...	1.59 $J_{\text{H}_{\text{A}}-\text{H}_{\text{B}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{B}'}} = 14$ $J_{\text{H}_{\text{A}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{C}}} = 13$ $J_{\text{P}-\text{H}_{\text{A}}} =$ $J_{\text{P}-\text{H}_{\text{A}'}} < 1$	2.05 $J_{\text{H}_{\text{B}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{B}'}-\text{H}_{\text{C}}} = 7$	1.90 $J_{\text{P}-\text{H}_{\text{C}}} = 6$ $J_{^{195}\text{Pt}-\text{H}_{\text{C}}} =$ 40	7.8-7.2, Ph
2b^f	8.1 (d)	1905 (trans to C)	17	3.01 $J_{\text{H}_{\text{A}}-\text{H}_{\text{B}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{B}'}} = 12$	2.03 $J_{\text{H}_{\text{B}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{B}'}-\text{H}_{\text{C}}} = 7$	1.51 $J_{\text{P}-\text{H}_{\text{C}}} = 8$	7.8-7.2, Ph 1.85, Me
	3.1 (d)	4134 (trans to Cl)	17	$J_{\text{H}_{\text{A}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{C}}} = 13$ $J_{\text{P}-\text{H}_{\text{A}}} =$ $J_{\text{P}-\text{H}_{\text{A}'}} = 6$	$J_{\text{P}-\text{H}_{\text{B}}} =$ $J_{\text{P}-\text{H}_{\text{B}'}} \leq 1$	$J_{^{195}\text{Pt}-\text{H}_{\text{C}}} =$ 42	1.27, Me' $J_{\text{P}-\text{H}(\text{Me})} =$ $J_{\text{P}-\text{H}(\text{Me}')} =$ 9.6 $J_{^{195}\text{Pt}-\text{H}(\text{Me})} =$ 25 $J_{^{195}\text{Pt}-\text{H}(\text{Me}')} =$ 45
2c^g	15.54	2677	...				
2d^f	57.6 (d)	1951 (trans to Cl)	10	2.92 $J_{\text{H}_{\text{A}}-\text{H}_{\text{B}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{B}'}} = 11.5$	2.01 $J_{\text{H}_{\text{B}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{B}'}-\text{H}_{\text{C}}} = 5$	2.11 $J_{\text{P}-\text{H}_{\text{C}}} = 7$	7.8-7.2, Ph 7.2-6.6, C_2H_2
	49.6 (d)	4016 (trans to Cl)	10	$J_{\text{H}_{\text{A}}-\text{H}_{\text{C}}} =$ $J_{\text{H}_{\text{A}'}-\text{H}_{\text{C}}} = 13$ $J_{\text{P}-\text{H}_{\text{A}}} =$ $J_{\text{P}-\text{H}_{\text{A}'}} = 5$	$J_{\text{P}-\text{H}_{\text{B}}} =$ $J_{\text{P}-\text{H}_{\text{B}'}} \leq 1$	$J_{^{195}\text{Pt}-\text{H}_{\text{C}}} =$ 43	

^a ± 0.1 ppm; (d), doublet; other resonances, singlets. ^b ± 4 Hz. ^c See Figure 2 for subscript notations for cyclopentyl protons. ^d ± 0.03 ppm. ^e ± 0.5 Hz. ^f All $J_{\text{P}-\text{H}}$ values refer to P trans to cyclopentyl. ^g In C_6H_6 solution; from ref 24. ^h ^1H NMR spectrum not listed since signals of cyclopentyl H's masked by those of c-Hx, H's.

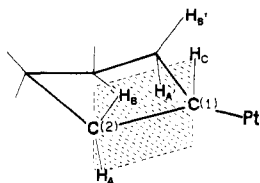


Figure 2. Proposed structure of the $\text{C}_3\text{H}_5\text{-TCNE}$ moiety from ^1H NMR.

reactions of platinum(II) complexes are catalyzed by the presence of potentially coordinating ligands.

A representative 270-MHz ^1H NMR spectrum of the cycloadducts, that of **2b**, is shown in Figure 1 as spectrum A. The five protons of the cyclopentyl ligand give rise to three separate groups of signals, I, II, and III, with intensity ratios of 2:2:1. This part of the spectrum may be interpreted on the basis of an AA'BB'C spin system, additionally interacting with the ^{31}P and ^{195}Pt nuclei. A good agreement between the experimental and simulated spectra has been achieved with the data reported in Table IV. This is illustrated by spectra A (experimental) and B (simulated) for **2b** in Figure 1. The subscript notations used for the various hydrogens of the cyclopentyl ring are those shown in Figure 2.

Free rotation around the Pt-C σ bond renders isochronous but not magnetically equivalent the two protons A and A' as well as B and B'. Protons AA' and BB' are differently coupled to the central proton C, $J_{\text{H}_{\text{A}(\text{A}')}-\text{H}_{\text{C}}}$ and $J_{\text{H}_{\text{B}(\text{B}')}-\text{H}_{\text{C}}}$ being 13 and 5-7 Hz, respectively. These data suggest that protons BB' may lie markedly out of the plane defined by H_{C} , C(1), and C(2) (or C(5)) in Figure 2, whereas

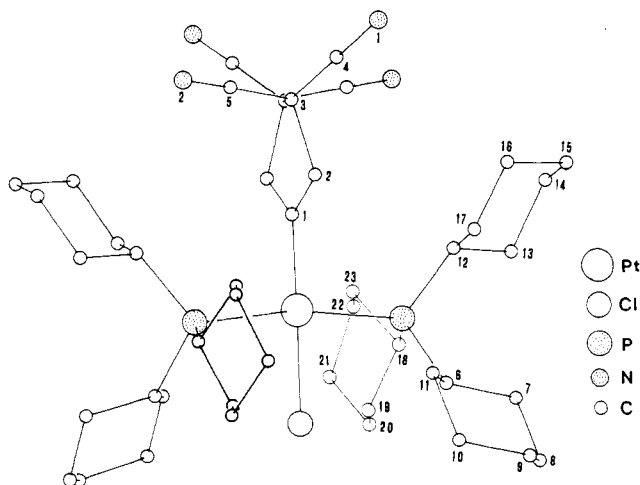


Figure 3. Molecular structure of **2c**, with the numbering scheme. The unnumbered phosphine is related to the numbered phosphine by a twofold axis passing through the Pt-C bond.

protons AA' may occupy positions near this plane. As a consequence, the resulting structure of the $\text{CH}_2\text{C}(\text{CN})_2\text{-C}(\text{CN})_2\text{CH}_2\text{CH}$ ligand should be strongly asymmetric. The X-ray structural determination confirms this interpretation.

Description of Structures. The molecular structures of **2c** and **2d** are shown in Figures 3 and 4, respectively, with the atoms being systematically numbered. Bond lengths and angles of interest are listed in Table V for **2c**

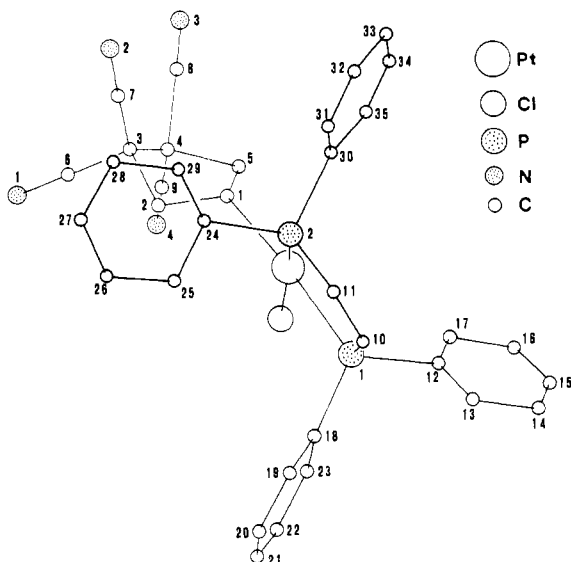


Figure 4. Molecular structure of 2d, with the numbering scheme.

Table V. Bond Lengths and Angles for 2c, with Estimated Standard Deviations in Parentheses^a

(a) Bond Lengths (Å)			
Pt-P	2.368 (7)	C(3)-C(3')	1.78 (4)
Pt-Cl	2.412 (8)	C(3)-C(4)	1.49 (4)
Pt-C(1)	2.06 (3)	C(3)-C(5)	1.48 (4)
C(1)-C(2)	1.57 (4)	av P-C	1.89 (2)
C(1')-C(2)	1.51 (5)	av C-N	1.12 (3)
C(2)-C(3)	1.63 (4)	av C-C	1.57 (3)

(b) Bond Angles (deg)			
P-Pt-Cl	84.9 (1)	C(2)-C(1)-C(2')	110 (3)
P-Pt-P'	169.8 (2)	C(1)-C(2)-C(3)	102 (2)
P-Pt-C(1)	106 (1)	C(2)-C(3)-C(3')	100 (2)
P-Pt-C(1')	84 (1)	C(2)-C(3)-C(4)	110 (2)
Cl-Pt-C(1)	169 (1)	C(2)-C(3)-C(5)	114 (2)
Pt-P-C(6)	109.3 (9)	C(3')-C(3)-C(4)	108 (2)
Pt-P-C(12)	120.0 (9)	C(3')-C(3)-C(5)	112 (2)
Pt-P-C(18)	111.5 (8)	av C-P-C	105 (4)
Pt-C(1)-C(2)	116 (2)	av P-C-C	111 (5)
Pt-C(1)-C(2')	119 (3)	av C-C-C	110 (3)
		av C-C-N	177 (3)

^a Primed and nonprimed atoms are related by $-x, y, 1/2 - z$. For P-c-Hx₃ and CN, average values (av) are given with the standard deviation of the mean in parentheses.

and Table VI for 2d. Least-squares planes are given in Table VII.

The structure of each complex consists of discrete monomeric molecules with a grossly approximated square-planar geometry about the platinum center. In 2c the coordinating atoms are coplanar within 0.014 Å with platinum. The two Pt-P bonds are symmetry equivalent, and the distance of 2.368 (7) Å appears to be among the longest found in trans-bis(phosphine) complexes of platinum(II), where the Pt-P bond lengths fall in the range 2.23–2.37 Å.^{12,40,41} It is comparable to the very long distance of 2.359 (4) Å observed for the Pt-PPh₃ bonds in 1a.⁸ The observed long Pt-P bond distance in 2c is most likely caused by steric interactions between the bulky P-c-Hx₃ groups and the cyclopentyl ligand. This is supported by the marked deviation from 90° of the valence angles around platinum, viz., P-Pt-P = 169.8 (2)°, P-Pt-Cl = 84.9 (1)°, and P-Pt-C(1) = 106 (1)° (see Figure 5A).

Table VI. Bond Lengths and Angles for 2d, with Estimated Standard Deviations in Parentheses^a

(a) Bond Lengths (Å)			
Pt-P(1)	2.288 (4)	C(4)-C(5)	1.60 (3)
Pt-P(2)	2.183 (4)	C(3)-C(6)	1.43 (3)
Pt-Cl	2.362 (4)	C(3)-C(7)	1.53 (3)
Pt-C(1)	2.13 (2)	C(4)-C(8)	1.44 (3)
P(1)-C(10)	1.81 (2)	C(4)-C(9)	1.47 (3)
P(2)-C(11)	1.81 (2)	C(10)-C(11)	1.36 (2)
C(1)-C(2)	1.53 (3)	av P-C	1.83 (1)
C(1)-C(5)	1.57 (3)	av C-N	1.14 (1)
C(2)-C(3)	1.58 (2)	av C-C	1.38 (3)
C(3)-C(4)	1.56 (3)		

(b) Bond Angles (deg)			
P(1)-Pt-P(2)	86.7 (2)	Pt-C(1)-C(2)	110 (1)
P(1)-Pt-Cl	94.2 (2)	Pt-C(1)-C(5)	115 (1)
P(1)-Pt-C(1)	174.9 (5)	C(1)-C(2)-C(3)	104 (1)
P(2)-Pt-Cl	176.7 (2)	C(2)-C(3)-C(4)	102 (1)
P(2)-Pt-C(1)	88.7 (5)	C(2)-C(3)-C(6)	117 (2)
Cl-Pt-C(1)	90.4 (5)	C(2)-C(3)-C(7)	109 (2)
Pt-P(1)-C(10)	107.2 (5)	C(4)-C(3)-C(6)	114 (2)
Pt-P(1)-C(12)	117.2 (6)	C(4)-C(3)-C(7)	107 (2)
Pt-P(1)-C(18)	117.8 (5)	C(6)-C(3)-C(7)	107 (2)
C(10)-P(1)-C(12)	105.8 (8)	C(3)-C(4)-C(5)	105 (1)
C(10)-P(1)-C(18)	102.9 (8)	C(3)-C(4)-C(8)	114 (1)
C(12)-P(1)-C(18)	104.4 (7)	C(3)-C(4)-C(9)	108 (2)
Pt-P(2)-C(11)	109.6 (6)	C(5)-C(4)-C(8)	113 (2)
Pt-P(2)-C(24)	110.9 (5)	C(5)-C(4)-C(9)	109 (1)
Pt-P(2)-C(30)	119.0 (6)	C(8)-C(4)-C(9)	107 (2)
C(11)-P(2)-C(24)	106.7 (7)	C(1)-C(5)-C(4)	105 (1)
C(11)-P(2)-C(30)	103.3 (8)	av P-C-C	120 (2)
C(24)-P(2)-C(30)	106.5 (7)	av C-C-C	119 (4)
C(2)-C(1)-C(5)	106 (1)	av C-C-N	178 (1)

^a For PPh₃ and CN, average values (av) are given with the standard deviation of the mean in parentheses.

Table VII. Equations of Least-Squares Planes with Deviations (Å, in Square Brackets) of Atoms from Planes

2c	
Plane Pt, P, Cl, C(1)	$6.970x - 0.1127y + 10.63z = 2.624$ [Pt 0.009, P -0.001, Cl -0.004, C(1) -0.005]
2d	
Plane P(1), P(2), C(10), C(11)	$-7.518x + 2.801y + 16.43z = 1.021$ [Pt 0.020, P(1) 0.006, P(2) -0.006, C(10) -0.015, C(11) 0.015, Cl 0.180, C(1) 0.108]
Plane P(1), P(2), Cl, C(1)	$-7.405x + 3.521y + 16.49z = 1.161$ [Pt -0.053, P(1) -0.010, P(2) 0.011, Cl 0.009, C(1) -0.010]

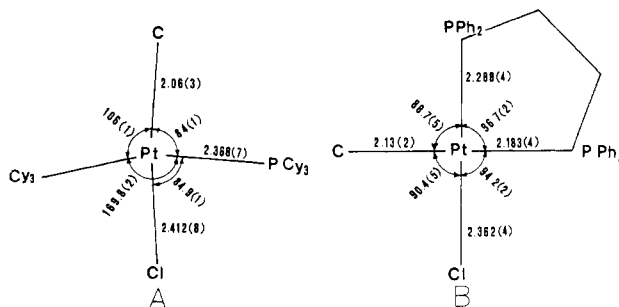


Figure 5. Coordination bond lengths and angles for (A) 2c and (B) 2d.

The Pt-Cl bond length of 2.412 (8) Å is unexceptional for complexes with a trans Cl-Pt-C donor atom system and reflects a large trans influence of the carbon-bonded ligand.¹² The Pt-C distance of 2.06 (3) Å is close to typical values of Pt(II)-C(sp³) bonds.^{12,42,43}

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In spite of the low accuracy of the structural determination owing to poor quality of obtainable crystals, the geometry of the $\overline{\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2\text{CH}}$ group was unequivocally established and found to be similar to that in **2d** (vide infra). However, the limits of error are too large to permit making a detailed comparison between the two structures.

Complex **2d** has the expected distorted square-planar geometry, with the diphosphine ligand occupying two cis positions. The Pt-P(2) bond length of 2.183 (4) Å (Figure 5B) is shorter than the lower limit in the range of known Pt(II)-P distances.^{40,43} This short Pt-P bond may result from an enhancement of Pt-to-P π bonding caused by the unsaturated nature of the chelating diphosphine. Such π bonding receives support from the observed coplanarity of the platinum center with the P(1), C(10), C(11), and P(2) atoms of the bidentate ligand. The Pt-P(1) distance of 2.288 (4) Å is longer than the aforementioned Pt-P(2) distance owing to a greater trans influence of the σ -C donor compared to that of Cl⁻. It represents a typical Pt(II)-P (trans to C) bond length.^{12,43}

The coordination environment of platinum, comprised of P(1), P(2), Cl, and C(1), is slightly distorted from planarity (within ± 0.01 Å), with the metal being 0.05 Å out of this plane. The Pt-Cl and Pt-C(1) bond distances of 2.362 (4) and 2.13 (2) Å, respectively, are unexceptional for platinum(II) complexes when positioned trans to a phosphine ligand.^{12,42,43}

The structural parameters of the cyclopentyl ring have "normal" values⁴⁴ and are comparable within experimental errors for the two compounds. Furthermore, they are similar to the parameters reported for the cyclopentyl ligand of $[(\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2\text{C}(\text{CH}_3))\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$.⁴¹ The major difference between the platinum and iron complexes concerns the geometry of the four cyclopentyl carbon atoms that are not bonded to the metal. In the iron complex they are approximately planar, whereas in the platinum complexes they are twisted around the central bond. Thus the torsion angles around the $\text{C}(\text{CN})_2\text{-C}(\text{CN})_2$ bond are 0.44 (molecule A) and -5.3° (molecule B) in the iron complex (values calculated from the parameters given in ref 44) and -33.0 and -33.6° in **2c** and **2d**, respectively.

It seems likely that the different conformation in the iron complex results from a compromise of repulsive interactions associated with the ligands, especially those involving the cyano groups and the methyl substituent on C(1). This causes the cyano groups to be nearly eclipsed. In the platinum complexes, which have H instead of CH₃ on C(1), the $\text{C}(\text{CN})_2\text{-C}(\text{CN})_2$ bond can assume the more favored staggered conformation. Furthermore, in the iron complex, the $\text{C}(\text{CN})_2\text{-C}(\text{CN})_2$ bond distance is 1.605 (3) and 1.593 (3) Å in the two crystallographically independent molecules.⁴⁴ This exceptionally large $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ distance has been attributed to a withdrawal of electron density from the bond in question by the cyano substituents. The effect is, however, surprisingly large. Unfortunately, the presence of very heavy atoms such as Pt did not allow an accurate determination of C-C bond lengths in **2c** and **2d**. However, in the more accurate structure of **2d**, the C(3)-C(4) bond distance of 1.56 (3) Å is close to the expected value. It is therefore possible that the C(C-

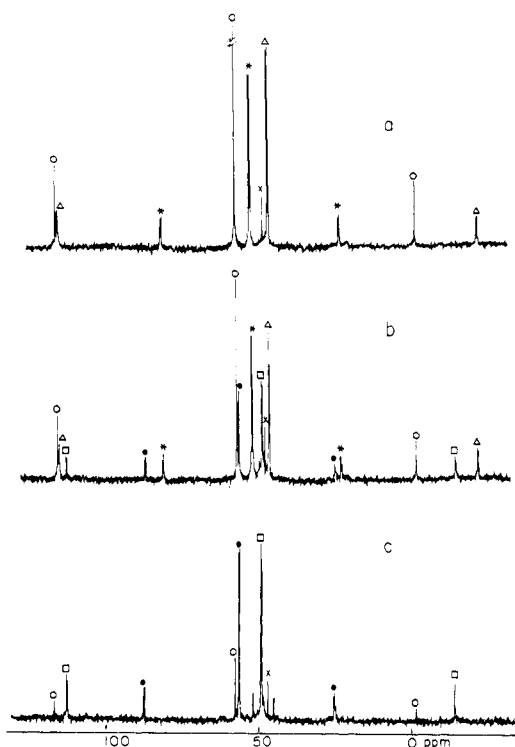


Figure 6. ^{31}P NMR spectra of **1d** reacting with TCNE in CD_2Cl_2 solution at -69 to -71 °C: (a) before addition of TCNE; (b) 100 min after addition of TCNE; (c) 210 min after addition of TCNE ((Δ) **1d**; (\circ) $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{Ph}_2\text{PCH}=\text{CHPh}_2)]^+\text{Cl}^-$; (\square , \bullet) **2d**).

$\text{N})_2\text{-C}(\text{CN})_2$ distance in the iron complex is unusually long not only because of the aforementioned electronic effect but also for steric reasons to alleviate repulsion between the eclipsed cyano groups.

^{31}P NMR Study of Cycloaddition. Progress of the cycloaddition reaction (eq 4) of each of **1a-d** was followed at low temperature by ^{31}P NMR spectroscopy in CD_2Cl_2 solution. The use of CD_2Cl_2 , in which the complexes **1a-d** are quite soluble, allowed the spectra of the reacting mixtures to be obtained in a relatively small number of scans. The spectra were recorded as often as needed to detect and monitor the fate of any reaction intermediates.

Representative spectra of the reacting system **1d** and TCNE are shown in Figure 6. On dissolution in CD_2Cl_2 at -69 to -71 °C, the platinum complex affords a 70:30 equilibrium mixture of the η^1 -allyl species **1d** and the η^3 -allyl species $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{Ph}_2\text{PCH}=\text{CHPh}_2)]^+\text{Cl}^-$ (Table III, Figure 6a). The spectrum recorded 100 min after addition of TCNE, also at -69 to -71 °C, shows the η^1 - and η^3 -allyl complexes in the same 70:30 ratio, together with a noticeable amount of the cycloaddition product **2d** (Figure 6b). Subsequent spectra indicate progressive conversion of the platinum-allyl species to **2d** (see Figure 6c). No other signals are observed in the course of the reaction. Increasing the temperature to -20 °C results in the disappearance of the signals owing to the formation of paramagnetic species, as the solution turns blue.

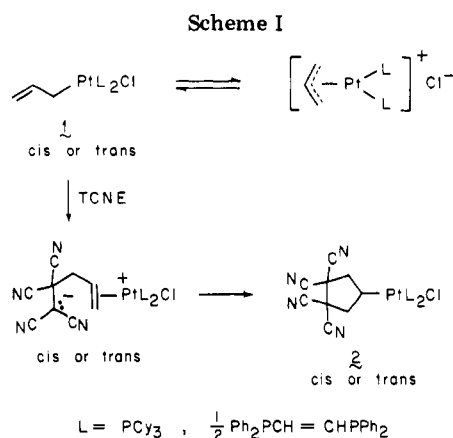
To determine which of the detectable platinum-allyl complexes is the reactive species, we allowed $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{Ph}_2\text{PCH}=\text{CHPh}_2)]^+\text{BF}_4^-$ to interact with TCNE under comparable experimental conditions. No reaction was observed. However, addition of $[\text{As}(n\text{-Bu})_4]^+\text{Cl}^-$ to the reaction mixture in question leads to the formation of **2d** as described above.

The spectrum of a mixture of **1c** and TCNE, recorded 30 min after the preparation of the solution in CD_2Cl_2 at -69 to -71 °C, shows only the presence of **2c**. Again, the

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(43) Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevuto, V.; Romeo, R.; Belluco, U. *Inorg. Chim. Acta* 1978, 31, 171.

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η^3 -allyl complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{P-c-Hx}_3)_2]^+\text{B}_4^-$ is unreactive toward TCNE, but the addition of $[\text{As}(n\text{-Bu})_4]^+\text{Cl}^-$ restores the reactivity described for **1c**.

The foregoing results demonstrate that **1c** and **1d**, rather than $[(\eta^3\text{-C}_3\text{H}_5)\text{PtL}_2]^+$ (L = P-c-Hx₃ and 0.5Ph₂PCH=CHPh₂, respectively), are the active platinum complexes in the cycloaddition reaction. Addition of $[\text{As}(n\text{-Bu})_4]^+\text{Cl}^-$ to $[(\eta^3\text{-C}_3\text{H}_5)\text{PtL}_2]^+\text{BF}_4^-$ converts these η^3 -allyl cations to **1c** and **1d** (see eq 3), thus allowing the reaction to proceed. Although no direct mechanistic inferences can be drawn from these ³¹P NMR data, we believe that TCNE reacts with **1c** and **1d** by electrophilic attack at the allylic double bond, as shown in Scheme I. The suggested mechanism is comparable to that proposed for the reactions of the 18-electron transition-metal- η^1 -allyl complexes with various unsaturated electrophiles, E=Nu.^{6,7} This supposition is influenced by consideration of steric properties of **1c** and **1d**, both of which are crowded around the central platinum atom.⁸ Thus, it would appear that the terminus of the η^1 -allyl ligand is the most vulnerable site for attack by TCNE. Dissociation of the phosphine from **1c** and **1d** and coordination of TCNE may be ruled out from the ³¹P NMR data.

In contrast to the aforementioned behavior of **1c** and **1d** toward TCNE, reactions of each of **1a** and **1b** with TCNE proceed via spectroscopically detectable intermediates. ³¹P NMR spectra of the reacting system **1b** and TCNE in CD₂Cl₂ solution at low temperature are shown in Figure 7. Complex **1b** undergoes virtually complete conversion to $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{PMePh}_2)_2]^+\text{Cl}^-$ on dissolution in CD₂Cl₂ at -69 to -71°C (Table III). Addition of TCNE to this solution gradually leads to the appearance of a signal of another species A with δ 0.0 and $J_{195\text{Pt-P}} = 3639$ Hz in the ³¹P NMR spectrum. Figure 7a shows the spectrum that was recorded 20 min after the addition of TCNE; the ratio of $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{PMePh}_2)_2]^+\text{Cl}^-$ to A is 70:30. On storage of the solution, this ratio decreases to 40:60 after 60 min (Figure 7b) and, after ca. 90 min the starting η^3 -allyl complex is almost completely consumed. The temperature was then raised to -48 to -50°C, and the solution was examined (Figure 7c) 15 min later (105 min after the addition of TCNE). Species A has been largely converted (ca. 50%) to yet another species B, characterized by the signals at δ -4.3 (d) and -6.4 (d), coupled together ($J_{\text{P-P}} = 21$ Hz) and to ¹⁹⁵Pt ($J_{195\text{Pt-P}} = 3494$ and 3577 Hz, respectively). Also observable in this spectrum are the resonances of the cycloadduct **2b** at δ 3.2 (d) and 8.2 (d), but the corresponding ¹⁹⁵Pt satellites are too weak to be seen. The spectrum in Figure 7d was recorded 150 min after the addition of TCNE and with the temperature raised to -25 to -28°C; it shows a larger amount of **2b** and B and a substantial decrease in the amount of A. Con-

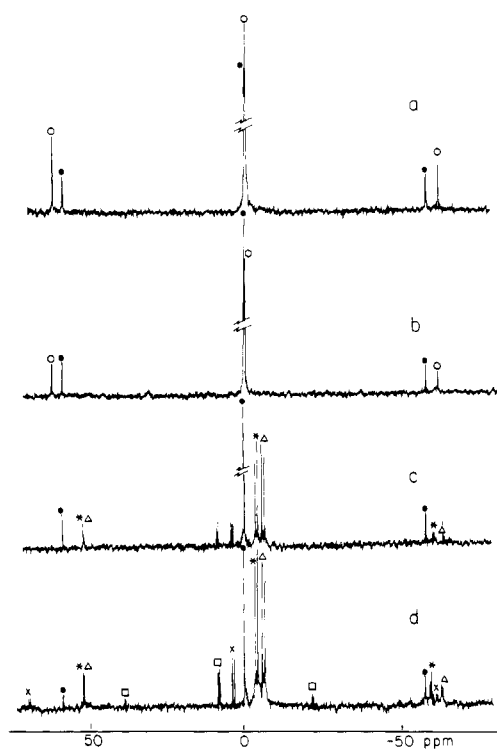


Figure 7. ³¹P NMR spectra of **1b** reacting with TCNE in CD₂Cl₂ solution: (a) 20 min after addition of TCNE, at -69 to -71°C; (b) 60 min after addition of TCNE, at -69 to -71°C; (c) 105 min after addition of TCNE, at -48 to -50°C; (d) 150 min after addition of TCNE, at -25 to -28°C. ((O) $[(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{PMePh}_2)_2]^+\text{Cl}^-$; (●) intermediate A; (*, Δ) intermediate B; (□, X) **2b**).

tinued storage of the solution at this temperature leads to the formation of additional **2b**. However, when the temperature was further raised to -10°C, the solution turned blue and the signals disappeared.

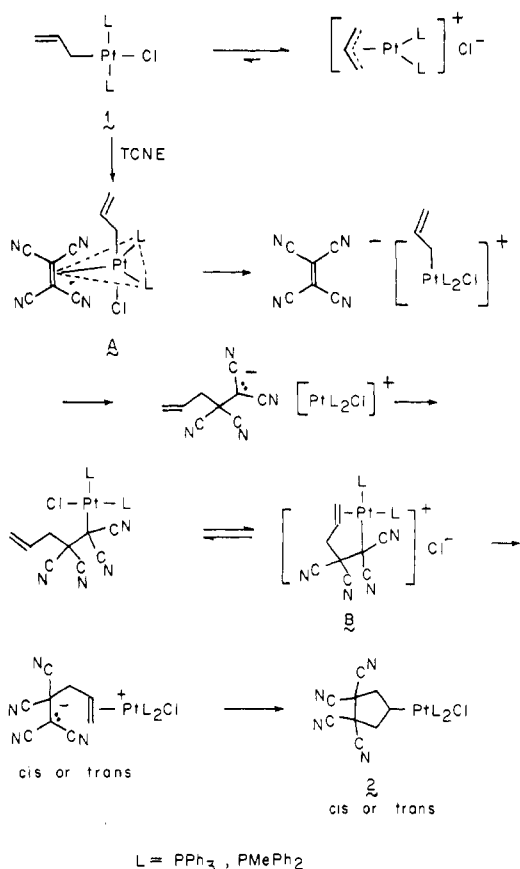
A similar ³¹P NMR behavior was noted when a solution containing **1a** and TCNE in CD₂Cl₂ was stored at -69 to -71°C. Species analogous to A (A', δ 13.8 ($J_{195\text{Pt-P}} = 3681$ Hz)) and B (B', δ 6.4 (d) and 11.8 (d) ($J_{\text{P-P}} = 9$ Hz)) were formed in the course of the reaction that eventually yielded **2a**. However, unlike the conversion of **1b** to **2b**, the last observable step (i.e., B' to **2a**) occurred with a change in the relative positions of the two phosphines to afford a trans cycloadduct.

The corresponding $[(\eta^3\text{-C}_3\text{H}_5)\text{PtL}_2]^+\text{BF}_4^-$ (L = PPh₃ and PMePh₂) complexes, like their L = P-c-Hx₃ and 0.5Ph₂PCH=CHPh₂ analogues, were found to be unreactive toward TCNE under similar conditions. However, the addition of $[\text{As}(n\text{-Bu})_4]^+\text{Cl}^-$ immediately led to a reproduction of all of the features in the ³¹P NMR spectra of **1a** and **1b** reacting with TCNE.

Again, the above-described ³¹P NMR data implicate **1a** and **1b** as the actual reactants in cycloaddition, even though they are not spectroscopically detectable in solution. The fact that these η^1 -allyl complexes are less sterically encumbered than **1c** and **1d** and the fact that relatively long-lived intermediates are produced in reasonably high concentrations during the reaction both suggest that in these cases cycloaddition proceeds by attack of TCNE at the metal rather than the allylic terminus. Any plausible intermediates generated by the mechanism in Scheme I would not be expected to possess the values of $J_{195\text{Pt-P}}$ observed for A and B or to exhibit the stability of these two species.

A possible mechanism of these reactions is presented in Scheme II. It has evolved (i) on the assumption that

Scheme II



TCNE adds to the platinum center and (ii) in an attempt to provide rational intermediates for which the expected ³¹P NMR spectra are in accord with those observed for A and B. Accordingly, the trigonal-bipyramidal adduct of 1 with TCNE, in which the two phosphines are equivalent,

is designated as A. Further reaction by electron transfer followed by cleavage of the platinum- η^1 -allyl bond and combination of the ions affords a product of insertion of TCNE into the Pt-C linkage. This sequence is analogous to that proposed by Kochi for reactions of main-group metal-allyl compounds with TCNE.⁴⁵ Substitution of the allylic double bond for coordinated Cl⁻ would give a species with the expected ³¹P NMR spectroscopic properties similar to those of B.³⁷

In summary, it would appear that reactions of platinum(II)- η^1 -allyl complexes 1 with TCNE proceed by at least two pathways that are dependent on the nature of the ligated phosphine. Sterically encumbered complexes probably react by attack of TCNE at the peripheral allylic double bond, whereas the less crowded complexes may react by addition of TCNE to the metal. Studies are presently in progress on reactions of 1 with other electrophiles, E=Nu, to elaborate further the scope and mechanism of cycloaddition involving such 16-electron complexes.

Acknowledgment. We wish to acknowledge financial support of this investigation by NATO (Grant No. 068.81 to M.C., G.C., and A.W.), the National Science Foundation (Grant CHE-7911882 to A.W.), and the Ministero Pubblica Istruzione (Rome).

Registry No. 1a, 61374-44-5; 1b, 85168-56-5; 1c, 81111-59-3; 1d, 85168-57-6; 2a, 85168-58-7; 2b, 85168-59-8; 2c, 85201-90-7; 2d, 85168-60-1; [(η^3 -C₃H₅)Pt(PPh₃)₂]⁺BF₄⁻, 36484-04-5; [(η^3 -C₃H₅)Pt(PMePh₂)₂]⁺BF₄⁻, 36607-45-1; [(η^3 -C₃H₅)Pt(P(c-Hx)₃)₂]⁺BF₄⁻, 85168-61-2; [(η^3 -C₃H₅)Pt(Ph₂PCH=CHPh₂)]⁺BF₄⁻, 85168-63-4; [Pt(C₃H₅)Cl]₄, 32216-28-7; TCNE, 670-54-2.

Supplementary Material Available: Listings of structure factors for 2c and 2d (16 pages). Ordering information is given on any current masthead page.

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