

Preparation of Bis(η^3 -allyl)(tetracyanoethylene)platinum and Its Reaction with Triphenylphosphine Leading to the Addition of Both Allyl Groups to Tetracyanoethylene

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Received February 19, 1985

Tetracyanoethylene (TCNE) reacts with (η^3 -C₃H₅)₂Pt (1) to give the 1:1 adduct (η^3 -C₃H₅)₂Pt(TCNE) (2), the structure of which was inferred with the aid of low-temperature ¹H NMR spectroscopy. This adduct decomposes in the presence of an equimolar amount of PPh₃ to afford Pt metal and C₃H₅C(CN)₂C(CN)₂C₃H₅ (4), which is a product of linear addition of two allyl groups to TCNE. This same organic compound is obtained by reaction of a 1:1 adduct of 1 and PPh₃, (η^3 -C₃H₅)Pt(η^1 -C₃H₅)(PPh₃) (3), with an equimolar amount of TCNE. The foregoing reactions were studied by low-temperature ³¹P{¹H} and ¹H NMR spectroscopy; results indicate that PPh₃ displaces the TCNE in 2 to give 3. Complex 3 then reacts with TCNE via two successive observable intermediates, formulated as (η^3 -C₃H₅)Pt[C(CN)₂C(CN)₂C₃H₅](PPh₃) (5) and [η^4 -C₃H₅C(CN)₂C(CN)₂C₃H₅]Pt(PPh₃) (6), to afford Pt metal, PPh₃, and 4. A general mechanism is proposed for these reactions.

Introduction

Platinum complexes² offer a number of advantages in mechanistic studies of reactions that are catalyzed, or are germane to catalysis, by organometallic compounds. Generally, their stability compares favorably with that of related complexes of other transition metals. Moreover, the observation of ¹⁹⁵Pt coupling with the ¹H, ¹³C, or ³¹P nuclei in the NMR spectra often provides valuable, if not diagnostic, structural information. The elucidation by some of us³ of the mechanism of half-hydrogenation of dienes with (η^3 -C₃H₅)Pt(PR₃)₂H illustrates this point.

Recently we reported⁴ that 16-electron (η^1 -allyl)platinum(II) complexes, (η^1 -C₃H₅)Pt(PR₃)₂Cl, react with TCNE to give products of [3 + 2] cycloaddition, CH₂C(CN)₂C(CN)₂CH₂CHPt(PR₃)₂Cl. Since (η^1 -allyl)platinum(II) complexes often afford equilibrium mixtures containing (η^3 -allyl)platinum(II) species in solution,⁵⁻¹⁰ it was of interest to extend our investigation to the latter class of compounds. Accordingly, a study was undertaken on reaction of the 16-electron (η^3 -C₃H₅)₂Pt¹¹ (1) with TCNE. Herein we report on the formation of a 1:1 adduct of the foregoing reactants and on the behavior of this adduct toward PPh₃.

Experimental Section

Materials, Instrumentation, and General Procedures. All

chemicals were handled under an atmosphere of dry nitrogen. Solvents were carefully dried and purified by standard methods.¹² They were degassed by freeze-pump-thaw cycles before each reaction. (η^3 -C₃H₅)₂Pt (1) was obtained in pentane solution as described elsewhere.¹¹ The concentration of this solution was determined by treating a 5-mL aliquot with H₂ at 0 °C and analyzing Pt metal by atomic absorption spectroscopy. The standardized solution was kept in a Schlenk tube under nitrogen at -20 °C in the dark. All other chemicals were obtained from commercial sources and were used as received, except TCNE which was sublimed.

IR spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer in toluene solution with polystyrene calibration. ¹H NMR spectra were collected on a Varian Associates FT 80A or a Bruker 270 spectrometer; the reported values of *J* are accurate to ± 0.1 Hz. ³¹P{¹H} NMR measurements were performed on the Varian FT 80A at 32.203 MHz; the reported chemical shifts are with reference to 85% H₃PO₄ and are accurate to ± 0.05 ppm. Samples for NMR analysis were prepared by distilling deuterated solvent onto the compound(s) weighed in an NMR tube which, after degassing, was evacuated and sealed.

A Perkin-Elmer Series 2 liquid chromatograph equipped with an LC 75 spectrophotometric detector and a C₈ 25-cm preparative column was used for separation of reaction products. A Hewlett-Packard Model 5985B was employed for gas chromatographic-mass spectrometric analysis. (GC, injection temperature 250 °C, SE 54 25-m capillary column i.d. 0.3 mm, temperature range 90-220 °C, 7 °C/min; MS, source temperature 200 °C, 70 eV). Conductivity experiments were carried out by using an LKB Conductolyzer, type 5300B.

Preparation of (η^3 -C₃H₅)₂Pt(TCNE) (2). A solution of TCNE (0.256 g, 2 mmol) in toluene was added dropwise with stirring to an equimolar amount of (η^3 -C₃H₅)₂Pt (1) as 29.2 mM pentane solution (68.5 mL) under nitrogen at -20 °C. The resulting yellow solution afforded a yellow precipitate on storage for 2 days at -20 °C. The precipitate was filtered off at the same temperature, washed with pentane, and dried in vacuo. The yield of 2 was 0.74 g (91%). The product was recrystallized from toluene-pentane. Anal. Calcd for PtC₁₂H₁₀N₄: C, 35.56; H, 2.49; N, 13.82. Found: C, 35.6; H, 2.4; N, 14.1.

Preparation of (η^3 -C₃H₅)Pt(η^1 -C₃H₅)(PPh₃) (3). A solution of PPh₃ (0.270 g, 1.03 mmol) in hexane (50 mL) was added dropwise with stirring to an equimolar amount of (η^3 -C₃H₅)₂Pt (1) as 34.3 mM pentane solution (30 mL) under nitrogen at -70 °C. A white solid precipitated in 2 h and was filtered off to give 0.450 g (81%) of 3. Anal. Calcd for PtC₂₄H₂₅P: C, 53.43; H, 4.67. Found: C, 52.3; H, 4.8.

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Reaction of $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}(\text{TCNE})$ (2) with PPh_3 . A solution of 2 (0.320 g, 0.789 mmol) in CH_2Cl_2 (45 mL) was allowed to react with an equimolar amount of PPh_3 (0.207 g), which was added dropwise with stirring in the same solvent (30 mL) under nitrogen. After about 2 h of reaction time at room temperature, the solution precipitated Pt metal. This was removed by filtration through Florisil, and the clear filtrate was concentrated to ca. 10 mL. PPh_3 was separated from other components by HPLC with 3:1 $\text{CH}_3\text{-CN-H}_2\text{O}$ as the mobile phase at room temperature. Retention times were as follows: PPh_3 , 10.0 min; organic product (4), 12.5 min; flow rate, 1 mL/min. The solution of 4 was concentrated under reduced pressure to afford a pale yellow solid, which was recrystallized from CH_2Cl_2 -pentane and dried in vacuo. The yield of 4 was 0.120 g (73%). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_4$: C, 68.55; H, 4.79; N, 26.65. Found: C, 67.9; H, 4.9; N, 27.0.

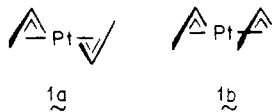
The foregoing reaction was repeated; however, the product mixture was maintained as a suspension for 6 h at room temperature. Under these conditions, both 4 and an isomer of it were isolated by GLC, the latter as a minor product. The two compounds analyzed as $\text{C}_{12}\text{H}_{10}\text{N}_4$ and displayed similar mass spectra. ^1H NMR of isomer of 4: δ 4.34 (center of apparent t); 2.52, 2.49, 2.46 (m); 2.31, 2.28, 2.25, 2.22, 2.20 (apparent quintet).

Reaction of $(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\eta^1\text{-C}_3\text{H}_5)(\text{PPh}_3)$ (3) with TCNE. A CH_2Cl_2 solution (60 mL) of 3 (0.431 g, 0.8 mmol) was treated under nitrogen at -20°C with TCNE (0.102 g, 0.8 mmol) dissolved in the same solvent. Slow precipitation of Pt metal occurred in 6 h at -20°C . Products were separated as in the reaction of 2 with PPh_3 (vide supra).

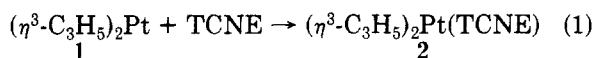
Progress of this and the preceding reaction was monitored in CD_2Cl_2 solution at -40°C by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

Results and Discussion

The complex $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$ (1), an equilibrium mixture of isomers **1a** and **1b**,^{13,14} reacts slowly with an equimolar



amount of TCNE in pentane solution at -20°C to give a unique adduct that analyzes as 2 (eq 1).



Product 2, a yellow solid, is fairly stable to air. Its IR spectrum in toluene solution shows a single ν_{CN} absorption at 2220 cm^{-1} , which militates against the presence of Pt-CN bonds¹⁵ and suggests a highly symmetric environment of TCNE. Conductivity measurements on ca. $2 \times 10^{-2}\text{ M}$ solutions of 2 in 1,2-dichloroethane and acetonitrile at 20°C furnished Λ_{M} values of 0.5 and $1.6\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, respectively, to rule out an ionic structure such as $[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}]^+\text{TCNE}^-$.¹⁶

The ^1H NMR spectrum of 2 in CD_2Cl_2 solution at -55°C , shown in Figure 1, provides the best evidence for the proposed structure. The allyl proton resonances appear in three regions, being centered at δ 2.98, 4.08, and 5.12. The signals at δ 2.98 are assigned to the equivalent anti protons ($J_{\text{H-H}_a} = 12.2$, $J_{\text{Pt-H}_a} = 53.5\text{ Hz}$), whereas those at δ 4.08 are assigned to the equivalent syn protons ($J_{\text{H-H}_s} = 7.1$, $J_{\text{Pt-H}_s} = 24.2\text{ Hz}$). The multiplet at δ 5.12, partly masked by the resonance of CH_2Cl_2 , is attributed to the

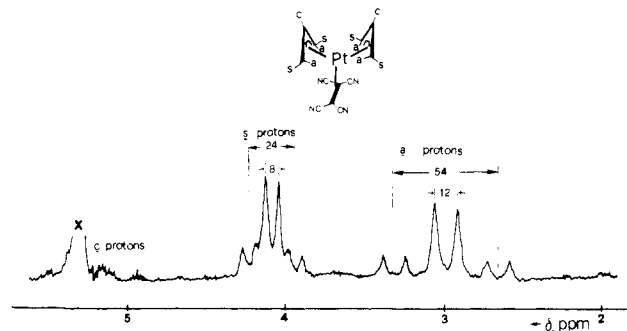
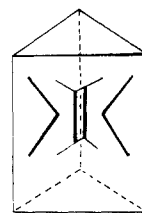


Figure 1. 270-MHz ^1H NMR spectrum of 2 in CD_2Cl_2 solution at -55°C . The labels s, a, and c stand for syn, anti, and central protons, respectively. X is the resonance of CH_2Cl_2 .

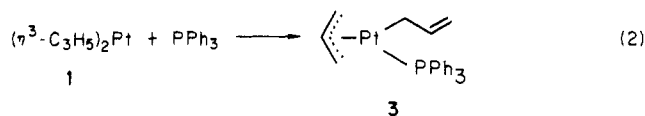
central proton of the allyl ligands. ^1H NMR spectra of 2 in the temperature range -75 to -55°C do not display any significant changes compared to the spectrum in Figure 1. As the temperature is raised above -55°C , the resonances centered at δ 2.98 and 4.08 broaden and, at 20°C , the spin-spin coupling disappears without changes in the chemical shifts.

The spectrum given in Figure 1 represents a typical $\text{A}_2\text{M}_2\text{X}$ ^1H NMR spectrum of $(\eta^3\text{-allyl})\text{metal complexes}$ ¹⁷ and indicates that the two $\eta^3\text{-C}_3\text{H}_5$ groups of 2 are equivalent. Consistent with this interpretation, the structure of 2 may be described in terms of the following quasi-trigonal-prismatic coordination



which is shown in more detail in the inset of Figure 1. This structural assignment accords with a recent theoretical investigation of $(\eta^3\text{-allyl})$ - and $(\eta^2\text{-alkene})\text{metal complexes}$.¹⁸ At room temperature, the observed spectral features suggest a slow exchange of the syn and anti protons. Such an exchange may occur either through in-plane rotation around the CH-CH_2 bond¹⁹ or via an $\eta^3 \rightleftharpoons \eta^1$ allyl mechanism.^{20,21}

Reaction of 1 with an equimolar amount of PPh_3 affords a white solid that analyzes as a 1:1 adduct of the two reactants, 3 (eq 2). The low-temperature (-76°C) $^{31}\text{P}\{^1\text{H}\}$



NMR spectrum of this product shows a resonance at δ 16.12 ($J_{\text{Pt-P}} = 3951\text{ Hz}$) which broadens at 0°C with disappearance of the $^{195}\text{Pt-P}$ coupling. No free PPh_3 is observed. The position of this resonance suggests an η^3, η^1 structure of 3, since complexes of general type $(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\text{PR}_3)\text{X}$ show value of $J_{\text{Pt-P}}$ in the range 3800–4000

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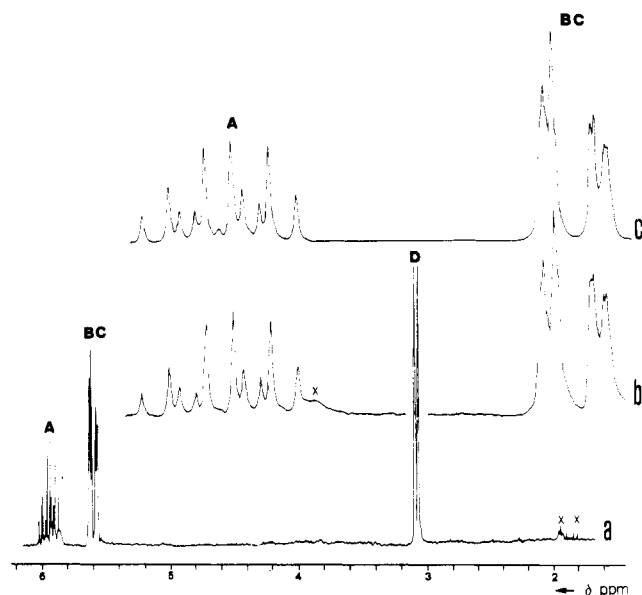
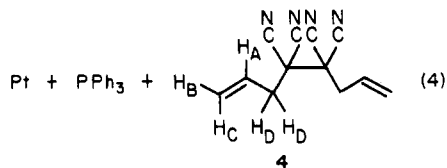
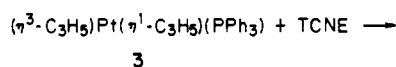
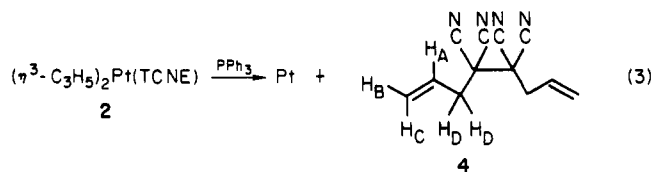


Figure 2. 270-MHz ^1H NMR spectra of **4**: (a) δ 1.5–6.2 region, CDCl_3 solution; (b) δ 5.5–6.1 region, CDCl_3 solution; (c) δ 5.5–6.1 region, simulated spectrum. The labels A, B, C, and D stand for the four sets of inequivalent protons of **4** shown in eq 3 and 4. X refers to impurities.

Hz ,^{3,4,7,8,22–24} The -76°C ^1H NMR spectrum of **3** shows the presence of coalescence broadened singlets at δ 5.02 (1 H), 3.74 (1 H), and 2.65 (1 H) and doublets at δ 3.89 (1 H, $J = 12.5$ Hz) and 3.07 (1 H, $J = 7.2$ Hz) which correspond to five allyl protons of an η^3 - C_3H_5 group. The spectrum also exhibits signals at δ 5.90 (1 H, m br), 5.57 (1 H, d, $J = 10.0$ Hz), 5.52 (1 H, d, $J = 14.5$ Hz), and 2.03 (2 H, m, $J = 7.5$ Hz, $J_{\text{Pt-H}} = 106$ Hz) which may be assigned to five allyl protons of an η^1 - C_3H_5 group.^{7–10,22–24} When the temperature is raised to -50°C , a complex pattern of signals arises which we cannot unambiguously interpret. It is likely that **3** undergoes intramolecular $\eta^3 \rightleftharpoons \eta^1$ allyl equilibria analogous to those of $(\eta^3\text{-C}_3\text{H}_5)\text{Pt}(\eta^1\text{-C}_3\text{H}_5)(\text{PMe}_3)$.²⁵

Both reactions of **2** with PPh_3 and of **3** with TCNE lead to decomposition of the starting complexes with the formation of Pt metal and an organic product, **4**, according to eq 3 and 4, respectively. No $\text{Pt}(\text{PPh}_3)_n$ complexes were



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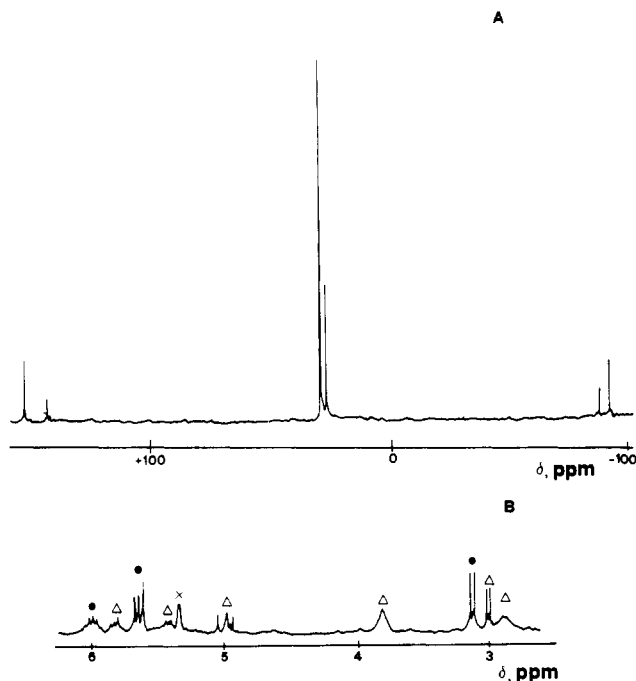


Figure 3. NMR spectra of equimolar amounts of **2** and PPh_3 reacting in CD_2Cl_2 solution at -40°C : (A) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after 15 min; (B) ^1H NMR spectrum after 127 min. Signals marked \bullet , Δ , and X are assigned to **6**, **5**, and CH_2Cl_2 , respectively.

observed in these reactions, probably owing to the 1:1 Pt: PPh_3 molar ratios employed. Compound **4** was separated from PPh_3 by HPLC; it was characterized by elemental analysis and ^1H NMR and mass spectroscopy. The ^1H NMR spectrum is shown in Figure 2, where the four sets of inequivalent protons are designated as ABCD₂. Decoupling experiments and spectrum simulation of the A + BC signals, the latter shown in Figure 2c, have allowed us to make the following assignments: δ_{H_A} 6.00, $\delta_{\text{H}_B} = \delta_{\text{H}_C}$ 5.62, δ_{H_D} 3.09; $J_{\text{H}_A\text{-H}_B} = 10.1$, $J_{\text{H}_A\text{-H}_C} = 16.5$, $J_{\text{H}_A\text{-H}_D} = 7.1$, $J_{\text{H}_B\text{-H}_C} = 1.0$, $J_{\text{H}_C\text{-H}_D} = 0.8$ Hz. The mass spectrum of **4** showed a molecular weight of 120, consistent with the proposed formulation.

When product mixtures of the reactions in eq 3 and 4 are set aside for several hours before workup, both **4** and another organic compound can be isolated. The latter, a minor product, is isomeric with **4** as indicated by elemental analysis and a mass spectrometric molecular weight determination. It appears that this compound, possibly 3,3,4,4-tetracyanobicyclo[4.2.0]octane, arises by slow isomerization of **4** which may be catalyzed by Pt metal.

Progress of the reactions depicted in eq 3 and 4 was examined by low temperature $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The objective of this study was to gain insight into the mechanism of this transformation which may be related to a number of oligomerization and oligomerization reactions catalyzed by allylmetal complexes.^{26–29}

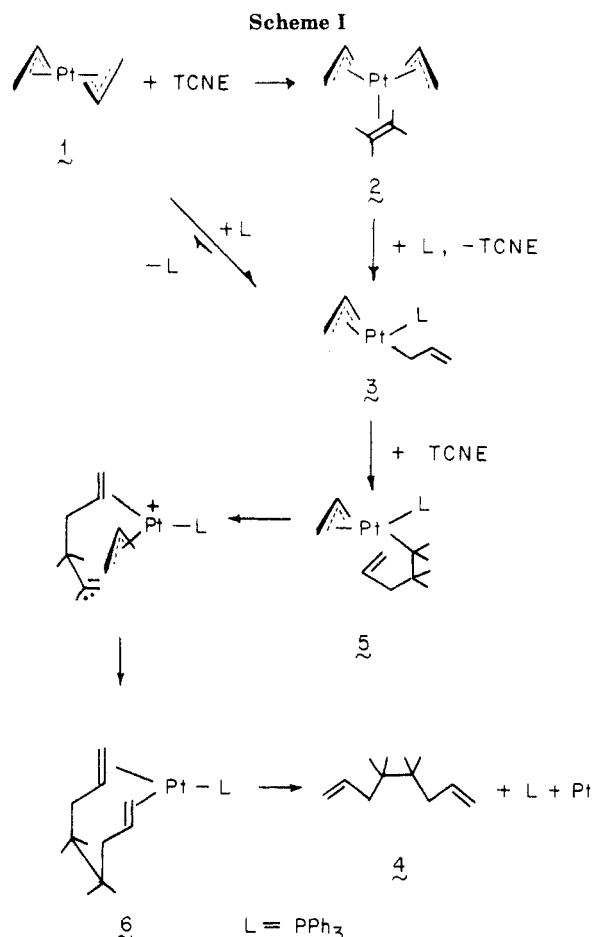
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reacting equimolar amounts of **2** and PPh_3 in CD_2Cl_2 solution at -40°C , recorded after 15 min of reaction time, is presented in Figure 3A. The absence of a signal at δ -5.25 indicates that all of the PPh_3 is coordinated to Pt. Two resonances of the

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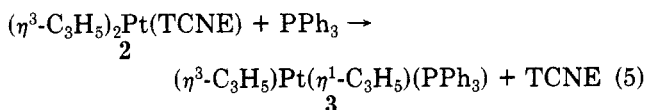
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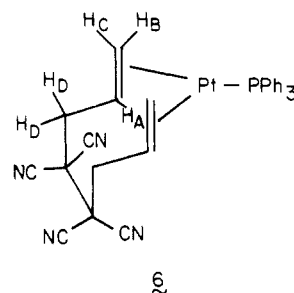


respective relative intensities 4:1 are observed in the spectrum: the resonance at δ 16.12 ($J_{Pt-P} = 3951$ Hz) indicates the presence of **3** whereas that at δ 15.18 ($J_{Pt-P} = 3747$ Hz) belongs to another intermediate, possibly having structure **5** (see Scheme I).³⁰ Identical results are obtained when **3** reacts with 1 molar equiv of TCNE under similar conditions. Thus, it may be reasonably proposed that attack of PPh_3 on **2** leads to a substitution reaction according to eq 5. Reaction of **3** with TCNE is then responsible for the formation of the final products in both cases.



After 2 h of reaction time at -40 °C, the mixture showed a new signal at δ 20.30 which is assigned to intermediate **6**, in addition to the signal of **5** and the much weaker signal of **3**, the ratio **6**:**5**:**3** being 5:4:1. At this stage of reaction, a 270-MHz 1H NMR spectrum of the solution was recorded possibly to help in the characterization of the intermediate species. It is shown in Figure 3B. Despite its complex nature, the spectrum allows an identification to be made of those signals (marked ●) that display a pattern analogous to that of the organic product **4** shown in Figure 2. These (●) signals, observed at δ 6.01 (center of m, protons

(30) A reviewer suggested that complex **5** may be alternatively formulated as a cycloaddition product, $(\eta^3-C_3H_5)PtCHCH_2C(CN)_2C(CN)_2CH_2(L)$, which undergoes retro-cycloaddition in rearranging to the next intermediate in Scheme I. We think that this possibility is unlikely, since $PtCHCH_2C(CN)_2C(CN)_2CH_2$ cycloaddition complexes show the 1H NMR resonance of PtCH at δ 2.2–1.5,⁴ and the region δ 2.5–0.0 is clear in the present spectrum.



A), 5.62 (center of m, protons B and C), and 3.12 (d, $J_{H_A-H_D} = 7.1$ Hz, protons D), have been assigned to species **6** containing coordinated **4**. The formation of free **4** at this stage of reaction is ruled out by the absence of Pt metal and free PPh_3 . Moreover, the resonances of the $CH=CH_2$ groups appear to be of a more complex nature for **6** compared to **4**. This difference may be ascribed to changes in geometry of **4** on coordination and to possible occurrence of $^{195}Pt-H$ coupling. In addition, coordination geometry of **6** is almost certainly more complex than that implied by its idealized structure, and rapid equilibria among species with different arrangements of ligand **4** are possible. Some support for this rationale is provided by the absence of ^{195}Pt satellites on the ^{31}P signal at δ 20.30. Other signals (marked Δ) in the spectrum in Figure 3B are probably associated with complex **5**, with much weaker resonances of **3** being lost in the background. Unfortunately, a reliable assignment of these resonances is precluded owing to the difficulties in carrying out a detailed 1H NMR analysis of a mixture of reacting species that are undoubtedly involved in rapid intra- and/or intermolecular equilibria.

The final step of the reactions in eq 3 and 4 was observed by increasing the temperature to -20 °C. The signal at δ 20.30 broadens, and the appearance of a new signal at δ -5.25 indicates the presence of free PPh_3 . This decomposition appears to be catalyzed by released phosphine. After the signal at δ -5.25 grows in, the rate of decomposition to Pt metal increases, thus preventing further monitoring of the reaction by NMR spectroscopy.

On the basis of the foregoing $^{31}P\{^1H\}$ and 1H NMR results we propose the sequence of reactions shown in Scheme I for the conversion of **1** to **4** and Pt metal by the action of PPh_3 and TCNE. As mentioned earlier (vide supra), the reactions leading to decomposition have been shown to proceed via interaction of **3** with TCNE to give an intermediate that is tentatively formulated as **5**. A similar intermediate derived by insertion of TCNE into a $Pt-(\eta^1-C_3H_5)$ bond was previously proposed for cycloaddition reactions of $(\eta^1-C_3H_5)Pt(PR_3)_2Cl$ with TCNE.⁴ Complex **5** may then rearrange to the dipolar intermediate shown in Scheme I in a reaction that is also analogous to that proposed for $(\eta^1-C_3H_5)Pt(PR_3)_2Cl$ and TCNE.⁴ For the latter system, the negative end of the zwitterion apparently attacks the terminal carbon of the η^2 -alkene fragment to furnish cycloaddition product. In the system under study, there is no evidence of such an interaction. Instead, the negative terminus of the dipolar complex would attack carbon 1 of the η^3 -allyl ligand leading to the formation of the diene **4** coordinated to Pt in complex **6**. This latter reaction would result in the formal reduction of platinum(II) in the zwitterionic complex (and also in **3** and **5**) to platinum(0) in **6**. On warming, **6** decomposes to **4**, Pt metal, and PPh_3 .

Notwithstanding rather tentative formulation of the intermediates detected in the formation of **4** from **2** and PPh_3 or from **3** and TCNE, the observed linear addition of two allyl groups to TCNE represents a reaction of some interest. This is largely because metal-promoted carbon-

carbon bond-forming reactions are of considerable general importance to organic synthesis.³¹ The present reaction affords the addition product 4 in good yield and without accompanying side processes. Cycloaddition of TCNE to coordinated allyl, observed for $(\eta^1\text{-C}_3\text{H}_5)\text{Pt}(\text{PR}_3)_2\text{Cl}$,⁴ does not occur here. The use of bis(allyl)metal complexes in the development of these and related co-oligomerization

reactions, and mechanistic studies of such processes, are under continuing investigation.

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

Registry No. 1a, 75110-81-5; 1b, 75110-82-6; 2, 98689-94-2; 3, 98689-95-3; 4, 98704-14-4; 5, 98689-96-4; 6, 98689-97-5; TCNE, 670-54-2; PPh₃, 603-35-0; Pt, 7440-06-4; 3,3,4,4-tetracyanobicyclo[4.2.0]octane, 98704-15-5.

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Chromium Tricarbonyl Complexes of Estradiol Derivatives: Differentiation of α - and β -Diastereoisomers Using One- and Two-Dimensional NMR Spectroscopy at 500 MHz

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Received May 24, 1985

The steroidal hormone β -estradiol and its derivatives in which the hydroxyl functionalities have been protected by benzyl or dimethyl-*tert*-butylsilyl groups bond to a tricarbonylchromium moiety via either the α - or the β -face of the arene ring. Unambiguous differentiation of these diastereomers is difficult without recourse to X-ray crystallographic techniques. These molecules have been characterized by 500-MHz ¹H and 125-MHz ¹³C NMR spectroscopy; assignments are made by using the two-dimensional techniques COSY and SECSY as well as heteronuclear shift-correlated spectra. Thus, high field NMR spectroscopy provides a straightforward method of differentiating between the α - and β -isomers.

Introduction

The biochemical importance of steroidal hormones which have been modified by the incorporation of organometallic moieties has only recently been appreciated. These species can function as markers in the study of receptors;¹ they are useful in immunology² and also serve as synthetic intermediates in regio- and stereospecific functionalizations.³ It is of course well documented that such organometallic complexes are of great synthetic utility, but they also show promise of unprecedented applications in the field of molecular biology.¹ This promise is founded first on the ability of metal carbonyl derivatives of hormones to recognize their specific receptor and secondly on the strong absorptions of the carbonyl ligands in the infrared region 2100–1850 cm⁻¹; this frequency range is compatible with a window in which the proteins do not absorb. This concept opens new vistas whose full potential can hardly be ascertained at present. We note that this extension beyond the normal realm of transition-metal complexes and into bioorganometallic chemistry has only become viable with the advent of Fourier transform infrared techniques which lowers the threshold of detection of so labeled hormones to the level of a few femtomoles per milligram of protein.¹ This concentration corresponds

to that commonly encountered in biological systems and so could be used to monitor the hormone dependence of breast cancer. Nevertheless, in spite of this enormous potential, there are still very few studies reported on these complexes.⁴ In particular, the complexation of the arene ring of estradiol and its derivatives with a tripodal group, such as Cr(CO)₃, is a diastereogenic reaction. The organometallic moiety can bind either to the " α " or to the " β " face of the hormone, as shown below.

The structure of the free hormone has been established by X-ray techniques⁵ but there are presently insufficient data to allow unambiguous structural assignments of or-

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