mmol), CH_2Cl_2 (20 mL), and a stir bar. The solution was cooled to −50 °C, then $Me_3SiOSO_2CF_3$ (0.270 mL, 1.400 mmol) was added. The reaction mixture was stirred for 1 h at −50 °C. Solvent was removed at room temperature in vacuo. The residue was extracted with pentane (2 × 5 mL). Removal of the solvent gave **6** (0.463 g, 1.190 mmol, 85%). NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 56.2 (d, $^3J_{PP}$ = 25.0 Hz, PC), 92.2 (d, $^3J_{PP}$ = 25.0 Hz, NP); ^1H NMR δ 1.08–1.34 (CH_3CH), 3.49 (m, CH_3CH), 9.14 (dd, $^2J_{HP}$ = 64.0 Hz, $^3J_{HP}$ = 30.0 Hz, HC=N); $^{13}C\{^1H\}$ NMR δ 24.45, 24.55, 24.63, 24.76, 24.87, 24.97, 25.02, 25.31 (s, CH_3CH), 46.37 (d, $^2J_{CP}$ = 12.0 Hz, CH_3CH), 49.48 (d, $^2J_{CP}$ = 10.0 Hz, CH_3CH), 178.60 (d, $^1J_{CP}$ = 23.0 Hz, HC=N). Mass spectrum: *m/e* 489. Anal. Calcd for $C_{25}H_{57}N_5P_2$: C, 61.32; H, 11.73. Found: C, 61.22; H, 11.61.

Preparation of $(i\text{-}Pr_2N)_2PC(H)=NB(N\text{-}i\text{-}Pr_2)_2$ (7). In a procedure analogous to that given for **4**, **3** prepared in situ in a toluene (40 mL) solution (**1** 1.26 g, 4.90 mmol: **2** 1.26 g, 4.89 mmol), was treated with a toluene (10 mL) solution of $(i\text{-}Pr_2N)_2BCl$ (1.21 g, 4.90 mmol) to give, after stirring 70 h, **7** (1.90 mg, 4.04 mmol, 83%) as a red-brown oil. NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 61.2 (s); ^{11}B NMR δ 31.8 (s); ^1H NMR δ 1.04–1.34 (CH_3CH), 3.43 (m, CH_3CH), 8.89 (d, $^2J_{HP}$ = 74.6 Hz, HC=N); $^{13}C\{^1H\}$ NMR δ 22.86, 23.45, 23.61, 23.97, 24.15, 24.55, 24.85, 25.18, 25.52 (s, CH_3CH), 46.20, 47.45 (s, CH_3CHNB), 47.72 (d, $^2J_{CP}$ = 11.6 Hz, CH_3CHNP), 49.93 (d, $^2J_{CP}$ = 9.6 Hz, CH_3CHNP), 170.58 (d, $^1J_{CP}$ = 6.0 Hz, HC=N); IR ν(C=N) 1657 (m) cm^{-1}. Mass spectrum: *m/e* 469. Anal. Calcd for $C_{19}H_{43}N_4P_2$: C, 58.59; H, 11.13. Found: C, 58.47; H, 11.02.

Preparation of $(i\text{-}Pr_2N)_2PC(H)=NBCl[N(SiMe_3)N(SiMe_3)_2]$ (8). In a procedure analogous to that given for **4**, **3** (0.487 g, 0.940 mmol), prepared in situ in toluene (4 mL), was treated with a toluene (8 mL) solution of $(Me_3Si)_2N(Me_3Si)NBCl_2$ (0.311 g, 0.940 mmol) to give, after stirring 30 min at −40 °C, **8** (0.440 g, 0.790 mmol, 85%) as a beige powder. NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 58.2 (s); ^{11}B NMR (C_6D_6) δ 31.4 (s); ^1H NMR (C_6D_6) δ 0.23 (s, $NSiCH_3$), 0.32 (s, $BNSiCH_3$), 0.97–1.23 (CH_3CH), 3.30 (m, CH_3CH), 9.20 (d, $^2J_{HP}$ = 49.9 Hz, HC=N); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 22.61, 23.06, 23.51, 24.03, 24.32, 24.61, 24.92, 25.14, 25.47 (s, CH_3CH), 50.07 (d, $^2J_{CP}$ = 12.4 Hz, CH_3CH), 50.12 (d, $^2J_{CP}$ = 10.0 Hz, $CH_3(CH)$, 184.34 (d, $^1J_{CP}$ = 8.8 Hz, HC=N). Mass spectrum: *m/e* 469. Anal. Calcd for $C_{19}H_{43}N_4P_2$: C, 58.59; H, 11.13. Found: C, 58.47; H, 11.02.

Registry No. **1**, 97135-49-4; **2**, 37342-97-5; **3**, 136044-16-1; **4**, 136044-18-3; **5**, 136044-19-4; **6**, 136044-20-7; **7**, 136044-21-8; **8**, 136044-22-9; **12**, 136044-23-0; **13**, 4791-48-4; **14**, 136044-17-2; Ph_2PCl, 1079-66-9; $(i\text{-}Pr_2N)PCl_2$, 921-26-6; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2; $Me_3SiOSO_2CF_3$, 27607-77-8; $(i\text{-}Pr_2N)_2BCl$, 28049-80-1; $(Me_3Si)_2NN(SiMe_3)BCl_2$, 136044-24-1; Me_3SnCl, 1066-45-1.

Synthesis, NMR Studies, and Reactions with Tetracyanoethylene of (η^1-Allyl)(aryl)platinum(II) Complexes

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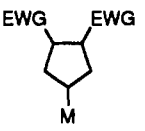
Summary: Some (η^1-allyl)(aryl)platinum(II) complexes of the type Pt(η^1-$CH_2CR{=}CH_2$)(Ar)(diphos) (R = H, Me; Ar = C_6F_5, $C_6H_3Cl_2$-2,5; diphos = $Ph_2PCH_2CH_2PPh_2$, (p-tol)$_2PCH_2CH_2P$(p-tol)$_2$) have been prepared from the corresponding η^3-allyl complexes Pt(η^3-CH_2CRCH_2)(Ar)(PPh$_3$) and diphosphines. ^1H NMR spectra of the 2,5-dichlorophenyl analogues were interpreted by occurrence of a restricted rotation of the aryl group about the Pt–C(Ar) bond. NOE experiments on the $CH_2CMe{=}CH_2$ derivatives suggested the occurrence of one dominant rotamer with regard to rotation about the C(α)—C(β) bond where the $CH_2{=}C(\beta)—C(\alpha)$ plane is nearly perpendicular to the Pt—C(α)—C(β) plane. Reactions of tetracyanoethylene with the η^1-$CH_2CH{=}CH_2$ analogues afforded formal [2 + 3] cycloadducts, whereas the reactions with the η^1-$CH_2CMe{=}CH_2$ analogues led to formation of linear adducts containing a $PtC(CN)_2C(CN)_2CH_2CMe{=}CH_2$ linkage.

The η^1-allyl ligand bound to transition metals is known to be susceptible to the attack of electrophilic olefins, primarily resulting in the formation of [2 + 3] cycloadducts **1**.[1] Of the group 10 metal allyl analogues, platinum derivatives were shown to adopt the η^1-allyl form with the greatest ease,[2] and thus their reactions with the olefins were studied in more detail than for the palladium and nickel derivatives.[3-5] One class of the (η^1-allyl)platinum(II) complexes studied has the general formula Pt(allyl)(Cl)(PR$_3$)$_2$, in which the reactive η^1-allyl form Pt(η^1-allyl)(Cl)(PR$_3$)$_2$ exists only as an equilibrium mixture with the cationic η^3-allyl form [Pt(η^3-allyl)(PR$_3$)$_2$]$^+$Cl$^-$, even



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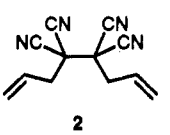

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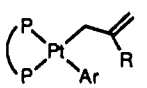

3a: R = H, Ar = C_6F_5, P⌒P = dppe
b: R = H, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dppe
c: R = H, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dtpe
d: R = Me, Ar = C_6F_5, P⌒P = dppe
e: R = Me, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dppe
f: R = Me, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dtpe

dppe = $Ph_2PCH_2CH_2PPh_2$; dtpe = (p-tol)$_2PCH_2CH_2P$(p-tol)$_2$

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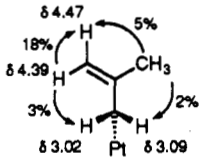
Table I. Relevant ^1H and ^{31}P NMR Spectral Data for (η^1-Allyl)platinum(II) Complexes[a]

	δ(H)					δ(P)	
complex	$PtCH_2$		=CR-	$=CH_2$		trans to Ar	trans to CH_2
3a	2.82 q (J_H = J_P = 8.5, J_{Pt} = 90)		6.18 m	4.37 dt (J_H = 16, J_P = 4, J_{Pt} = 24)	4.54 dt (J_H = 9.4, J_P = 3, J_{Pt} = 21)	−95.2 m (J_{Pt} = 2630)	−96.9 s (J_{Pt} = 1690)
3b[b]	2.98 m (J_{Pt} = 96)	3.05 m (J_{Pt} = 96)	6.28 m	4.56 d (J_H = 16, J_{Pt} = 28)	4.67 dt (J_H = 11, J_P = 3, J_{Pt} = 27)	−96.6 s (J_{Pt} = 2120)	−97.8 s (J_{Pt} = 1753)
3c[c]	3.03 m (J_{Pt} = 98)	3.11 m (J_{Pt} = 98)	6.34 m (J_H = 8, 10, 17)	4.66 dt (J_H = 17, J_P = 4, J_{Pt} = 27)	4.72 dt (J_H = 10, J_P = 4, J_{Pt} = 27)	−98.1 s (J_{Pt} = 2137)	−98.6 s (J_{Pt} = 1750)
3d	2.86 t (J_P = 9, J_{Pt} = 90)		1.68 s	4.29 s (J_{Pt} = 21)	4.36 s (J_{Pt} = 20)	−94.8 m (J_{Pt} = 2590)	−96.4 s (J_{Pt} = 1670)
3e[d]	2.97 dt (J_H = 10, J_P = 6, 10, J_{Pt} = 93)	3.03 q (J_H = 10, J_P = 10, 10, J_{Pt} = 99)	1.67 s	4.30 t (J_P = 3, J_{Pt} = 22)	4.41 s (J_{Pt} = 22)	−96.7 s (J_{Pt} = 2086)	−97.5 s (J_{Pt} = 1728)
3f[e]	3.02 dt (J_H = 10, J_P = 6, 10, J_{Pt} = 93)	3.09 q (J_H = 10, J_P = 10, 10, J_{Pt} = 100)	1.78 s	4.39 s (J_{Pt} = 22)	4.47 s (J_{Pt} = 22)	−98.1 s (J_{Pt} = 2088)	−98.4 s (J_{Pt} = 1724)

[a] ^1H NMR data in C_6D_6, ^{31}P NMR data in $CDCl_3$. Chemical shifts are in ppm, with J values in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Multiplets due to PCH_2 in all of compounds **3** (δ ca. 1.5–2.0) and those due to Ph in **3a,b,d,e** (δ ca. 7–8) are omitted. [b] δ(*o*-H) of $C_6H_3Cl_2$: 7.68 (dd, J_H = 2.5, J_P = 7, J_{Pt} = 64). δ(*p*-H) of $C_6H_3Cl_2$: 6.83 (dd, J_H = 8, 2.5). δ(*m*-H) of $C_6H_3Cl_2$ overlapped with phosphine phenyl resonances. [c] δ(Me) of *p*-tolyl group: 2.02 (s), 2.07 (s), 2.07 (s), 2.09 (s). δ(*o*-H) of *p*-tolyl group: 7.35 (dd, J_H = 8, J_P = 10.5), 7.49 (dd, J_H = 8, J_P = 10.5), 7.61 (dd, J_H = 8, J_P = 10.5), 7.93 (dd, J_H = 8, J_P = 10.5). δ(*m*-H) of *p*-tolyl group: 6.90 (d, J_H = 8), 6.93 (d, J_H = 8), 7.01 (d, J_H = 8), 7.04 (d, J_H = 8). δ(*o*-H) of $C_6H_3Cl_2$: 7.69 (dd, J_H = 2.5, J_P = 7, J_{Pt} = 64). δ(*m*-H) of $C_6H_3Cl_2$: 7.13 (dd, J_H = 8.5, J_P = 3, J_{Pt} = 22). δ(*p*-H) of $C_6H_3Cl_2$: 6.86 (dd, J_H = 8.5, 2.5). [d] δ(*o*-H) of $C_6H_3Cl_2$: 7.57 (dd, J_H = 2.5, J_P = 7, J_{Pt} = 63). δ(*p*-H) of $C_6H_3Cl_2$: 6.81 (dd, J_H = 8.5, 2.5). δ(*m*-H) of $C_6H_3Cl_2$ overlapped with phosphine phenyl resonances. [e] δ(Me) of *p*-tolyl group: 2.03 (s), 2.07 (s), 2.08 (s), 2.09 (s). δ(*o*-H) of *p*-tolyl group: 7.38 (dd, J_H = 8, J_P = 10.5), 7.51 (dd, J_H = 8, J_P = 10.5), 7.58 (dd, J_H = 8, J_P = 10.5), 7.89 (dd, J_H = 8, J_P = 10.5). δ(*m*-H) of *p*-tolyl group: 6.91 (d, J_H = 8), 6.96 (d, J_H = 8), 7.01 (d, J_H = 8), 7.02 (d, J_H = 8). δ(*o*-H) of $C_6H_3Cl_2$: ca. 7.6 (overlapped with other resonances). δ(*m*-H) of $C_6H_3Cl_2$: 7.10 (dd, J_H = 8.5, J_P = 3, J_{Pt} = 22). δ(*p*-H) of $C_6H_3Cl_2$: 6.83 (dd, J_H = 8.5, 2.5).

Chart I. NOE for 3f



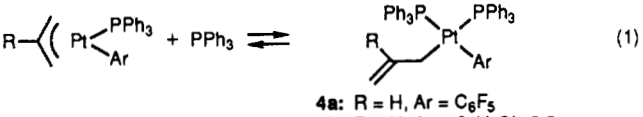
though a good yield of **1** was obtained in the end via the equilibrium shift $[Pt(\eta^3\text{-allyl})]^+ \rightarrow Pt(\eta^1\text{-allyl})(Cl)$.[3a] Another class of complexes without an ionizable chloride ligand, namely $Pt(\eta^1\text{-allyl})(\eta^3\text{-allyl})(PPh_3)$, also reacted with tetracyanoethylene.[3b] However, the product was not of the type **1** but the linearly coupled one **2**.

We have reported before that some palladium analogues $Pd(\eta^1\text{-allyl})(Ar)$(diphos) also reacted with maleic anhydride to give cycloadducts of the type **1**.[4] We now extend these studies to the platinum analogues $Pt(\eta^1\text{-allyl})(Ar)$(diphos) (**3**), which are stereochemically more rigid than both the palladium analogues and the two classes of (η^1-allyl)platinums shown above. We describe here the preparation and NMR studies of these new complexes and their reactions with tetracyanoethylene, which produced not only **1** but a linear adduct containing a $PtC(CN)_2C(CN)_2CH_2CMe{=}CH_2$ framework.

Results and Discussion

Synthesis and NMR Studies of η^1-Allyl Complexes. All of the (η^1-allyl)platinum(II) complexes **3** studied here were synthesized from the corresponding η^3-allyl analogues $Pt(\eta^3\text{-allyl})(Ar)(PPh_3)$ and the appropriate chelate diphosphine, as in the preparation of the (η^1-allyl)palladium(II) analogues.[2a,4] The ^1H and ^{31}P NMR spectra of these platinum complexes (see Table I) did not show any indication that a η^3-bound allyl form exists in the ground state or as a transient species. This result is in contrast to the spectral features of the palladium analogues[4] and the corresponding (η^1-allyl)(triphenylphosphine)platinum(II) analogues of type **4**, as discussed below.

We have found that the extent of the formation of the η^1-allyl species starting from $Pt(\eta^3\text{-allyl})(Ar)(PPh_3)$ and PPh_3 (eq 1) depends on the nature of the allyl substituent (R) and the aryl group ($CH_2CH{=}CH_2 > CH_2CMe{=}CH_2$; $C_6F_5 > C_6H_3Cl_2$-2,5), as confirmed by ^1H and ^{31}P NMR spectroscopy. Thus, the order of the stability of the



(1)

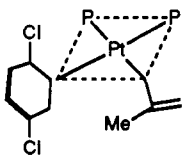
4a: R = H, Ar = C_6F_5
b: R = H, Ar = $C_6H_3Cl_2$-2,5
c: R = Me, Ar = C_6F_5
d: R = Me, Ar = $C_6H_3Cl_2$-2,5

η^1-allyl complex is **4a > 4b > 4c > 4d**. With the most favorable combination (allyl = $CH_2CH{=}CH_2$, Ar = C_6F_5) we previously isolated[2a] the stable η^1-allyl complex **4a**, but the other combinations resulted in incomplete formation of the η^1-allyl derivatives. In a previous paper[2a] we assigned the relative disposition of two molecules of PPh_3 in **4a** to be trans on the basis of the appearance of the $PtCH_2$ protons as a quartet (J_H = J_P = $J_{P'}$ = 8 Hz). However, the ^{31}P NMR spectrum now unambiguously shows that two phosphorus nuclei are inequivalent, with each of the two J_{Pt-P} values (1866 Hz, trans to CH_2; 2620 Hz, trans to C_6F_5, multiplet owing to couplings with ^{19}F) very similar to those of the chelate phosphine complex **3a** (1690, 2630 Hz), respectively. Thus, the cis structure of **4a** is quite evident. The other complexes of type **4** were also confirmed to have the cis structure by ^{31}P NMR spectra.[6]

Addition of PPh_3 to the corresponding (η^3-allyl)palladium(II) complexes $Pd(\eta^3\text{-allyl})(Ar)(PPh_3)$ (Ar = C_6F_5, $C_6H_3Cl_2$-2,5) did not give any clear NMR resonances assignable to η^1-allyl forms. However, examination of the

(6) Isolation of the analogous cis complex *cis*-$Pt(CH_3)(\eta^1\text{-}CH_2CH{=}CH_2)(PPh_3)_2$ has recently been reported: Suzuki, T.; Ueda, M.; Koumoto, R.; Nakamura, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 804.

Chart II



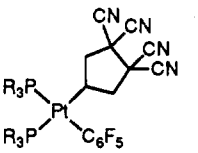
syn–anti proton exchange process in this system by the use of variable-temperature NMR methods suggested that the η^1-allyl form of the type Pd(η^1-allyl)(Ar)(PPh_3)$_2$ exists as a transient and this complex has predominantly the trans structure.[2a,7] The reason for the different geometry of M(η^1-allyl)(Ar)(PPh_3)$_2$ between M = Pd and M = Pt is not clear.[8]

^{1}H NMR spectral aspects of the 2,5-dichlorophenyl analogues **3b,c,e,f** deserve special comments. In these complexes, two proton signals of the $PtCH_2$ group appeared as nonequivalent to each other, while the corresponding protons in the pentafluorophenyl derivatives were equivalent. Raising the temperature of a toluene-d_8 solution of **3f** up to 105 °C did not cause any coalescence of the two inequivalent resonances. The origin of the magnetic nonequivalence of the CH_2 protons is most probably a restricted rotation of the 2,5-dichlorophenyl ring about the Pt–C(Ar) bond, with the aryl plane lying perpendicular to the coordination plane, thereby inducing asymmetry with respect to the coordination plane. This asymmetry then provides the molecule with chirality. This is further supported by the appearance of both aromatic and methyl protons of the *p*-tolylphosphine ligands of **3c,f** as four sets of resonances (Table I). The nonequivalent nature of the $PtCH_2$ protons in the dichlorophenyl analogues should in principle be retained even if the rotation of the η^1-allyl group about the Pt–C(α) bond takes place freely. However, this rotation would probably be restricted, for steric reasons, to a conformation in which the Pt–C(α)–C(β) plane is almost perpendicular to the coordination plane and the C(β) atom is on the opposite side of the ortho chloro substituent with respect to the coordination plane (see below).

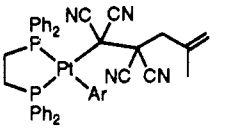
It seems of further interest to note that in the complex **3f** the methyl group appears to stay mostly in the position close to one of the $PtCH_2$ protons (δ 3.09), while the terminal vinyl group is in the position close to the other $PtCH_2$ protons (δ 3.02), as suggested by NOE experiments (see Chart I).[9] In the major conformation shown in Chart I, the dihedral angle between the Pt—C(α)—C(β) and the CH_2=C(β)—C(α) planes would be close to 90°, where the σ–π conjugation[10] in the (η^1-allyl)metal framework is expected to become maximum. In the rest of the time the complex might stay in another minor conformation(s) which has arisen from a rotation about the C(α)—C(β) bond of the major conformer shown in Chart I (see below). Analogous NOE experiments with the corresponding η^1-CH_2CH=CH_2 analogues **3b,c** suggested no such preference of a single conformer about the C(α)—C(β) axis, for the irradiation of either the –CH= proton or the terminal vinyl proton resulted in enhancement of both of the diastereotopic $PtCH_2$ proton intensities to almost the same degree (1% each).

With the C(α)—C(β) vector of **3e,f** fixed in one direction opposite to the ortho chloro substituent with respect to the coordination plane and with the CH_2=C(β)—C(α) plane perpendicular to the Pt—C(α)—C(β) plane, the ortho hydrogen atom of the $C_6H_3Cl_2$ ring would in the main be close to either the CH_3 or the =CH_2 protons. The NOE experiments[11a] suggest proximity of the CH_3 group to the $C_6H_3Cl_2$ ring (Chart II) at some stages. These experiments also suggest[11b] occurrence of the other minor conformer which results from the rotation about the C(α)—C(β) bond in Chart II by 180°. Low-temperature ^{1}H NMR experiments on **3f** showed that interconversion between these two conformers was not frozen at down to –90 °C in toluene-d_8 or CD_2Cl_2.

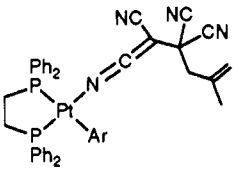
Reactions of (η^1-Allyl)platinum(II) Complexes with Olefins. The (η^1-allyl)platinum(II) complexes **3** did not react with maleic anhydride as readily as their palladium analogues did,[4] the latter having afforded [2 + 3] cycloadducts in moderate yields. In the present case, gradual formation of propene and isobutene, together with some unidentified products, began after ca. 1 day. With tetracyanoethylene **3a** gave the expected cycloadduct **5a** in 80% yield (in $CDCl_3$, 25 °C, 10 min). The similar adduct **5b** was also isolated (67%) from the PPh_3 analogue **4a** and tetracyanoethylene.



5a, 2 R_3P = dppe
b, R_3P = PPh_3



6a, Ar = C_6F_5
b, Ar = $C_6H_3Cl_2$-2,5



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In contrast to the behaviors of the η^1-CH_2CH=CH_2 complexes, the η^1-CH_2CMe=CH_2 complex **3d** reacted with tetracyanoethylene much more rapidly (almost 100% conversion, in $CDCl_3$, 25 °C, within 2 min) to give no cycloadduct but the conceivably linearly coupled adduct **6a** (^{1}H and ^{31}P NMR analysis). The dichlorophenyl analogue **3e** reacted with tetracyanoethylene in a similar way. Isolation of **6a,b** in a pure form was hampered by their thermal instability (a green color emerged in solution even shortly after the formation of **6**). In the ^{1}H NMR spectra,

(7) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333.

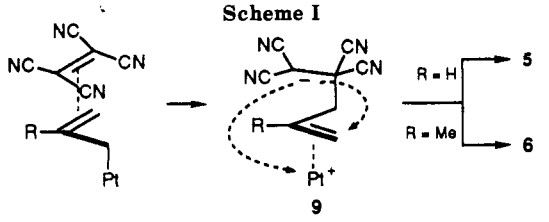
(8) (a) Note, however, that in dialkylplatinum complexes of the type Pt(R_2)(PR'_3)$_2$ the cis structure appears to be much more abundant than the trans structure, while both trans and cis forms exist equally in the case of the corresponding palladium complexes.[8b,c] (b) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 39. (c) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. Reference 8b, Chapter 38-4.

(9) Irradiation of the methyl protons resulted in an increase of the intensity of the resonance at δ 3.09 by 2% but only a slight increase of the intensity at δ 3.02, while the irradiation of the vinyl proton (δ 4.39) led to an increase of the resonance at δ 3.02 by 3% but an increase of that at δ 3.09 by less than 1%. The lower solubility of **3e** in benzene-d_6 precluded an exact estimation of the corresponding NOE values, but the trend was much the same. In $CDCl_3$ or CD_2Cl_2, the $PtCH_2$ proton signals overlapped with the PCH_2 proton signals at δ 2–2.5, as in all of the complexes of the type **3**.

(10) Brown, R. S.; Eaton, D. F.; Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* **1974**, *66*, 249 and references therein.

(11) (a) The experiments were conducted in CD_2Cl_2 because the resonance due to the ortho hydrogen of the $C_6H_3Cl_2$-2,5 ligand of **3f** in benzene-d_6 (δ ca. 7.6) overlapped with one of the *p*-tolyl ring proton resonances. Irradiation of this ortho proton of **3f** (δ 6.86 in CD_2Cl_2) resulted in an increase of the methyl signal intensity by 3%, but no increase of the vinyl proton signal intensities. The irradiation of the methyl signal in turn led to an increase of the ortho hydrogen signal intensity by 5%. Furthermore, the irradiation of the vinyl proton caused an increase of one of the ortho hydrogen signals of the *p*-tolyl groups at δ 7.47 by 3%. (b) The *p*-tolyl proton intensity (δ 7.47) also increased by ca. 1% when the methyl protons were irradiated.

Scheme I



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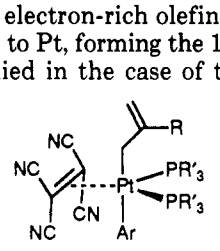
the CH_2 chemical shifts are in the range expected for the CH_2 group adjacent to the $C(CN)_2$ group when compared with the NMR data of analogous $C(CN)_2C(CN)_2CH_2R$ moieties,[12] and the appearance of the $CH_2CMe{=}CH_2$ proton resonances without any spin couplings with ^{31}P and ^{195}Pt nuclei is indicative of the cleavage of the Pt–allyl bond. Moreover, the appearance of the CH_2 protons in **6b** as a diastereotopic pair (see Experimental Section) is consistent with the restricted rotation of the aryl group. The ^{31}P resonance due to the phosphorus atom cis to the Ar group showed J_{Pt-P} values (3714 Hz for **6a**, 3950 Hz for **6b**) which are considerably larger than those for the complexes **3d** (1680 Hz) and **5a** (1880 Hz), suggesting binding of a ligand more electron withdrawing than the η^1-allyl carbon and cyclopentyl carbon atoms. These J_{Pt-P} values cannot distinguish between the structure **6** and its linkage isomer **7**, even though the IR spectra of crude solids of **6a** isolated at 0 °C showed no absorptions around 1300 cm^{-1} attributable to $\nu(N{=}C{=}C)$[12] of **7**; $\nu(C{\equiv}N)$ appeared at 2125 and 2175 cm^{-1}. It seems of further relevance to point out that $J_{Hg-H(^iPr)}$ for $^iPrHgC(CN)_2C(CN)_2{}^iPr$[12] and $J_{Tl-H(phenyl)}$ for $[PhTl\{CH(CN)_2\}(crown\ ether)]^+$,[13] both of which have been shown to contain a carbon-bound polycyanoalkyl ligand trans to the ^{i}Pr or Ph group, are close to or even greater than twice the corresponding J values for $^iPrHg^iPr$ and $[PhTl\{CH_2CH{=}CH_2\}(crown\ ether)]^+$, respectively.

The reactions of **3** with tetracyanoethylene may have proceeded as shown in Scheme I. The initial stage may well be a charge-transfer interaction between the electron-deficient and electron-rich olefins. Coordination of tetracyanoethylene to Pt, forming the 18-electron complex **8**, which was implied in the case of the reaction of Pt-



8

$(\eta^1$-allyl)(Cl)$(PR_3)_2$,[3a] may not be involved here in view of the fact that the sterically more demanding $CH_2CMe{=}CH_2$ complex reacted faster. One reason for the higher reactivity of this complex would be that the σ–π conjugation state (e.g. Chart I) is favored over the conformation in which the Pt—C(α)—C(β) plane is coplanar with the $CH_2{=}C(\beta){-}C(\alpha)$ plane to a greater extent in the $CH_2CMe{=}CH_2$ complex, due to the repulsion between Me and Pt, than in the $CH_2CH{=}CH_2$ complex. The electron-releasing nature of the methyl group may also contribute to greater stabilization of the charge-transfer state. Subsequent single-electron transfer and carbon–carbon bond formation would yield the intermediate **9**, from which was formed the cycloadduct in the case of the $CH_2CH{=}CH_2$ complex and the linear adduct in the case of the $CH_2CMe{=}CH_2$ complex. The cycloadduct formation from the latter complex would have been prevented by steric crowding at C(β).

Experimental Section

^1H and ^{31}P NMR spectra were obtained on JEOL GSX-400 and Bruker AM600 spectrometers at the Analytical Center, Faculty of Engineering, Osaka University. ^1H chemical shifts were measured relative to internal TMS and ^{31}P chemical shifts relative to external $P(OMe)_3$. Most of the commercially available reagents were used without further purification. Experiments employing organolithium reagents were performed under argon by using solvents which were dried by a sodium–benzophenone mixture prior to use. The preparation of $Pt(\eta^1\text{-}CH_2CH{=}CH_2)(C_6F_5)(PPh_3)_2$ and $Pt(\eta^1\text{-}CH_2CH{=}CH_2)(C_6F_5)$(dppe) was reported previously.[2a,4] 1,2-Bis(di-*p*-tolylphosphino)ethane was prepared from tri-*p*-tolylphosphine and sodium metal in liquid ammonia, followed by treatment with 1,2-dichloroethane.

Preparation of (η^3-Allyl)(aryl)platinum(II) Complexes. The $\eta^3\text{-}CH_2CMeCH_2$ complexes $Pt(\eta^3\text{-}CH_2CMeCH_2)(Ar)(PPh_3)$ (Ar = C_6F_5, $C_6H_3Cl_2$-2,5) were prepared from $Pt(\eta^3\text{-}CH_2CMeCH_2)(Cl)(PPh_3)$ and ArLi in a manner similar to that for the corresponding $\eta^3\text{-}CH_2CHCH_2$ analogues.[2a,14] $Pt(\eta^3\text{-}CH_2CMeCH_2)(C_6F_5)(PPh_3)$ (30%): pale yellow microcrystals; mp 168–170 °C. Anal. Calcd for $C_{28}H_{22}F_5PPt$: C, 49.49; H, 3.26. Found: C, 49.31; H, 3.32. ^1H NMR ($CDCl_3$): δ 1.96 (s, J_{Pt} = 52 Hz, 3 H), 2.30 (s, J_{Pt} = 44 Hz, 1 H), 2.47 (d, J_P = 10 Hz, J_{Pt} = 48 Hz, 1 H), 3.50 (br, 1 H), 3.75 (br, 1 H). $Pt(\eta^3\text{-}CH_2CMeCH_2)(C_6H_3Cl_2)(PPh_3)$ (45%): pale yellow powder; mp 169–170 °C dec. Anal. Calcd for $C_{28}H_{25}Cl_2PPt$: C, 51.07; H, 3.83. Found: C, 51.06; H, 3.90. ^1H NMR ($CDCl_3$): δ 1.97 (s, J_{Pt} = 50 Hz, 3 H), 2.36 (s, J_{Pt} = 38 Hz, 1 H), 2.4 (v br, 1 H), 3.29 (br, 1 H), 3.63 (br, 1 H).

Preparation of 3b–f. To a benzene solution (1 mL) of $Pt(\eta^3\text{-}CH_2CHCH_2)(C_6H_3Cl_2$-2,5)$(PPh_3)$ (87 mg; 0.135 mmol) was added dropwise dppe (54 mg; 0.136 mmol) in the same solvent (2 mL) at 5 °C. After the solution stood for 10 min, *n*-hexane was added so that pale yellow solids precipitated. These were recrystallized from benzene/*n*-hexane to give pale yellow microcrystals of **3b** (80%), mp 164 °C. Anal. Calcd for $C_{35}H_{32}P_2Cl_2Pt$: C, 53.86; H, 4.13. Found: C, 53.67; H, 4.26. Similarly prepared were the following. **3c** (78%): pale yellow microcrystals; mp 210 °C. Anal. Calcd for $C_{39}H_{40}P_2Cl_2Pt$: C, 55.99; H, 4.82. Found: C, 55.80; H, 4.61. **3d** (74%): pale yellow microcrystals; mp 195–196 °C. Anal. Calcd for $C_{36}H_{31}F_5P_2Pt$: C, 53.01; H, 3.83. Found: C, 53.45; H, 3.58. **3e** (75%): pale yellow microcrystals; mp 218–219 °C. Anal. Calcd for $C_{36}H_{34}P_2Cl_2Pt$: C, 54.42; H, 4.31. Found: C, 54.85; H, 4.22. **3f** (81%): colorless crystals; mp 179–181 °C. Calcd for $C_{40}H_{42}P_2Cl_2Pt$: C, 56.48; H, 4.98. Found: C, 56.52; H, 4.76.

NMR Examination of Equilibrium Mixture between Pt(η^3-allyl)(Ar)(PPh_3) and Pt(η^1-allyl)(Ar)$(PPh_3)_2$. In a typical procedure, the complex $Pt(\eta^3\text{-}CH_2CHCH_2)(C_6H_3Cl_2$-2,5)$(PPh_3)$ (10 mg; 0.0155 mmol) and an equimolar amount of PPh_3 were dissolved in 0.5 mL of $CDCl_3$ in an NMR tube. ^1H and ^{31}P NMR spectra were examined after ca. 30 min at 25 °C to show the existence of 25% of the η^3-allyl complex and 75% of **4b**. ^1H NMR ($CDCl_3$): δ 2.06 (m) and 2.25 (m) ($PtCH_2$), 3.55 (d, J_H = 18 Hz, =C*H*H), 4.07 (d, J_H = 13 Hz, =CH*H*), 5.40 (m, –CH=). ^{31}P NMR ($CDCl_3$): δ –118.1 (d, J_P = 13 Hz, J_{Pt} = 1956 Hz), –118.2 (d, J_P = 13 Hz, J_{Pt} = 2097 Hz). Similar experiments with $Pt(\eta^3\text{-}CH_2CHCH_2)(C_6F_5)(PPh_3)$ and PPh_3 revealed almost exclusive formation of **4a**.[2a] ^{31}P NMR ($CDCl_3$): δ –116.9 (m, J_{Pt} = 2620 Hz), –120.1 (d, J_P = 14 Hz, J_{Pt} = 1866 Hz). Similar NMR analysis of reactions of $Pt(\eta^3\text{-}CH_2CMeCH_2)(Ar)(PPh_3)$ with an equivalent amount of PPh_3 revealed the existence of the η^1-allyl form in ca. 17% for Ar = C_6F_5 and only ca. 5% for Ar = $C_6H_3Cl_2$-2,5. **4c**: ^1H NMR ($CDCl_3$) δ 1.14 (s, Me), 2.13 (t, J_P = 9 Hz, $PtCH_2$), 3.65 (s) and 3.75 (s) (=CH_2); ^{31}P NMR ($CDCl_3$) δ –117.5 (m, J_{Pt} = 2590 Hz), –120.4 (d, J_P = 16 Hz, J_{Pt} = 1860 Hz). **4d**: ^1H NMR ($CDCl_3$) δ 1.19 (s, Me), 2.14 (m) and 2.27 (m) ($PtCH_2$), 3.67 (s) and 3.82 (s) (=CH_2); ^{31}P NMR ($CDCl_3$) δ –118.7 (d, J_P = 13 Hz, J_{Pt} = 1935 Hz), –118.8 (d, J_P = 13 Hz, J_{Pt} = 2044 Hz).

(12) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 2460.
(13) Kawasaki, Y.; Akita, H.; Furuta, K.; Murai, S. Manuscript in preparation.
(14) Kurosawa, H.; Ishii, K.; Kawasaki, Y.; Murai, S. *Organometallics* **1989**, *8*, 1756.

Reaction of 3a with Tetracyanoethylene. To a benzene solution (1 mL) of **3a** (88 mg; 0.11 mmol) cooled to ca. 15 °C was added tetracyanoethylene (14.1 mg; 0.11 mmol). After the solution was kept at room temperature for 30 min, *n*-hexane was added so that colorless solids precipitated. These were recrystallized from benzene/*n*-hexane to give colorless solids of **5a** (72%): mp 188–189 °C. Anal. Calcd for $C_{41}H_{29}N_4F_5P_2Pt$: C, 52.97; H, 3.14; N, 6.03. Found: C, 53.03; H, 2.96; N, 5.98. ^{1}H NMR (C_6D_6): δ 1.5–1.65 (m, 4 H, PCH_2), 2.01 (m, 2 H), 2.5–2.6 (m, 3 H). ^{31}P NMR ($CDCl_3$): δ −97.0 (m, J_{Pt} = 2460 Hz), −97.5 (s, J_{Pt} = 1880 Hz).

Reaction of 4a with Tetracyanoethylene. The initial procedure was the same as that described above for **5a**. Upon addition of tetracyanoethylene, white solids precipitated, which were dissolved again by adding 2 mL of CH_2Cl_2. The solution was filtered, and *n*-hexane was added to the filtrate to give colorless microcrystals of **5b** (67%): mp 247–248 °C. Anal. Calcd for $C_{51}H_{35}N_4F_5P_2Pt$: C, 58.01; H, 3.34; N, 5.31. Found: C, 57.82; H, 3.06; N, 5.21. ^{1}H NMR ($CDCl_3$): δ 1.92 (m, 1 H), 2.09 (dd, J_H = 7.5, 13 Hz, 2 H), 2.46 (dt, J_H = 4.5, 13 Hz, 2 H). ^{31}P NMR ($CDCl_3$): δ −119.3 (m, J_{Pt} = 2460 Hz), −121.7 (d, J_P = 19 Hz, J_{Pt} = 2030 Hz).

Reactions of 3d,e with Tetracyanoethylene. The reaction was examined in an NMR tube containing a $CDCl_3$ solution (0.4 mL) of **3d** (9.5 mg; 0.011 mmol) and tetracyanoethylene (1.5 mg; 0.011 mmol). Two minutes after the substrates were dissolved, ^{1}H NMR measurements revealed the complete disappearance of the peaks due to **3d** and the appearance of new peaks at δ 1.81 (s, 3 H), 2.27 (m, 2 H), 2.40 (s, 2 H), 2.54 (m, 2 H), 4.95 (s, 1 H), 5.04 (s, 1 H). ^{31}P NMR ($CDCl_3$): δ −98.2 (m, J_{Pt} = 2230 Hz), −106.0 (d, J_P = 7 Hz, J_{Pt} = 3714 Hz). After ca. 10 min, the solution became green. ^{1}H NMR measurements after 1 day showed the disappearance of the resonances due to **6a** and the appearance of some unidentified peaks. In a similar reaction of **3e** with tetracyanoethylene in $CDCl_3$, approximately 70% formation of the linearly coupled product **6b** occurred in ca. 10 min. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 3 H), 2.17 (d, J_H = 14 Hz, 1 H), 2.28 (d, J_H = 14 Hz, 1 H), 2.2–2.5 (m, 4 H), 4.90 (s, 1 H), 5.01 (s, 1 H). ^{31}P NMR ($CDCl_3$): δ −99.1 (d, J_P = 6 Hz, J_{Pt} = 1890 Hz), −105.9 (d, J_P = 6 Hz, J_{Pt} = 3960 Hz).

Acknowledgment. Partial support of this work through Grants-in-aid from the Ministry of Education, Science and Culture of Japan is acknowledged.

Registry No. **3a**, 103836-52-8; **3b**, 136379-36-7; **3c**, 136379-37-8; **3d**, 136379-38-9; **3e**, 136379-39-0; **3f**, 136379-40-3; **4a**, 136458-37-2; **4b**, 136379-41-4; **4c**, 136379-42-5; **4d**, 136379-43-6; **5a**, 136379-44-7; **5b**, 136379-45-8; **6a**, 136379-46-9; **6b**, 136379-47-0; Pt(η^3-CH_2CHCH_2)($C_6H_3Cl_2$-2,5)(PPh_3), 136379-48-1; tetracyanoethylene, 670-54-2.