Insertion of Isocyanide into (σ-Allenyl)platinum(II) and -palladium(II) Compounds. Synthesis and Mechanism of Formation of New Organoplatinum Compounds Containing a σ-Bonded Vinylketenimine Ligand. X-ray Crystal Structure of [PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$]

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The insertion reactions of isocyanides into the metal-carbon bond of (σ-allenyl)platinum(II) and -palladium(II) complexes *trans*-[MX{C(H)=C=CRR''}(PPh$_3$)$_2$] (**1a-j**) are described. When the R groups of the allenyl ligand are small, these insertion reactions give rise to the formation of new (metallovinyl)ketenimine compounds *trans*-[MX{C(CRR')(CH=C=NR'')}(PPh$_3$)$_2$] (**2a-d**, **2i**, and **2j**). The platinum vinylketenimine complexes **2a-d** and **2i** are stable compounds, whereas the palladium vinylketenimine compound **2j** cannot be isolated. The structure of the (metallovinyl)ketenimine complexes has been confirmed by an X-ray crystal structure determination of *trans*-[PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$], **2a**: space group $P\bar{1}$, a = 11.907(2) Å, b = 12.603(2) Å, c = 14.862(3) Å, α = 81.74(2)°, β = 78.50(2)°, γ = 72.43(2)°, V = 2075.8(3) Å^3, Z = 2, R = 0.037, and R_w = 0.069. When the R groups of the allenyl ligand are large, the insertion of isocyanide is sterically hindered and the ionic complexes *trans*-[Pt{C(H)=C=CRR'}(CN-*t*-Bu)(PPh$_3$)$_2$]Br (**3e-h**) are formed. The mechanism of isocyanide insertions in (σ-allenyl)platinum(II) complexes was shown to be solvent dependent. When apolar or polar coordinating solvents were used, the reactions resulted in the formation of the platinum vinylketenimine complexes. When the reactions were performed in a polar noncoordinating solvent, or with (σ-allenyl)platinum(II) compounds containing large R groups, no formation of the platinum vinylketenimine complexes was observed, but the ionic [Pt{C(H)=C=CRR'}(CN-*t*-Bu)(PPh$_3$)$_2$]Br complexes were formed instead.

Introduction

The insertion of small molecules into metal-carbon bonds is an important reaction step in various homogeneously metal catalyzed syntheses of organic molecules.[1] In particular we are interested in the insertion of small molecules such as carbon monoxide and isocyanide into the metal-carbon bond of σ-allenyl-platinum and -palladium compounds. Insertion reactions of small molecules into σ-allenyl-metal complexes followed by a reductive elimination could give rise to unsaturated organic products, which maybe interesting starting compounds for fine chemicals. Recently, we reported the consecutive insertion of two molecules of carbon monoxide into (σ-allenyl)-palladium and -platinum compounds.[2] These reactions gave rise to the formation of (4-alkenyl-2(3*H*)-furanon-5-yl)bis(triphenylphosphine)platinum(II) and -palladium(II) bromides **D** (Scheme I).

The formation of **D** has been shown to take place via an insertion of CO into σ-allenyl complex **A**, resulting in the acyl complex **B**. Subsequently, a 1,3-metal shift gives the (metallovinyl)ketene complex **C**, which after a second CO insertion, a ring closure, and 1,4-H shift, is converted into furanonylmetal complex **D**. Intermediates **B** have been obtained as thermally stable and isolable compounds for M = Pt. The occurrence of the platinum vinylketene complex **C** as an intermediate has been substantiated by IR and NMR spectroscopy, but it could not be isolated.[2] It was argued that, when isocyanides are employed in insertion reactions with complex **A**, complex **E**, an analogue of complex **C**, would be formed. Probably, the (metallovinyl)ketenimine complex **E** is thermally more stable than **C**.

In this paper we present the study of the reactivity of (σ-allenyl)palladium and -platinum compounds toward isocyanides. The aim of this study involves (i) the elucidation of the mechanism of isocyanide insertion in square planar (σ-allenyl)palladium(II) and -platinum(II) compounds, (ii) the comparison between carbon monoxide and isocyanide insertion in these complexes, and (iii) the isolation of structural analogues of the (metallovinyl)-ketene **C**, *viz.* the (metallovinyl)ketenimines **E**.

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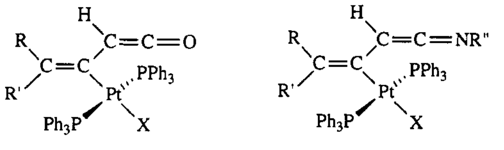
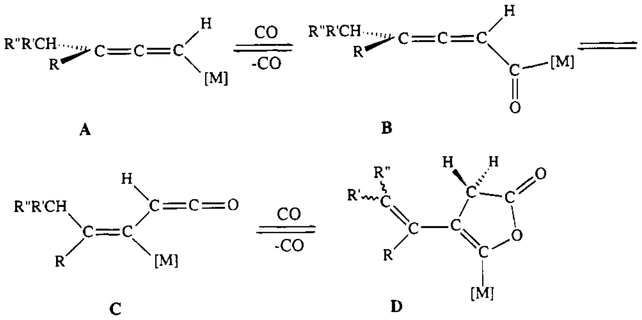


C E

Figure 1. Structurally analogous platinum vinylketene **C** and platinum vinylketenimine **E**.[2]

Scheme I. Proposed Mechanism for the Successive Insertion of Two Molecules of Carbon Monoxide into (σ-Allenyl)palladium and -platinum Complexes[a]



[a] [M] = Pt(PPh$_3$)$_2$Br or Pd(PPh$_3$)$_2$Br.

Experimental Section

General Considerations. Solvents were carefully dried and distilled prior to use. The reactions were performed under an atmosphere of dry nitrogen by using standard Schlenk techniques. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC 100, WM 250, and AMX 300 spectrometers, and infrared spectra were measured on Perkin Elmer 283 and Nicolet 7199B FT-IR spectrophotometers. Monitoring reactions with FT-IR spectroscopy were carried out in a so-called free access infrared (FAIR) cell.[3] Field desorption (FD) mass spectra were measured on a Varian Mat 711 double focusing mass spectrometer and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. Elemental analyses were carried out at the Analytical Department of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. The σ-allenyl starting compounds **1a–1i** were synthesized according to literature procedures.[4] *tert*-Butyl isocyanide and 2,6-xylyl isocyanide were purchased from Aldrich Chemie and were used without further purification.

Synthesis of (Metallovinyl)ketenimine Complexes 2a–d, 2i (M = Pt), and 2j (M = Pd). The synthesis of [PtBr{(Me$_2$C)C(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (**2a**) by the reaction of [PtBr(C(H)=C=CMe$_2$)(PPh$_3$)$_2$] (**1a**) and *tert*-butyl isocyanide is described in detail; the syntheses of **2b–d** were carried out analogously.

***trans*-[PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2a). A.** [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1a**) (366.4 mg, 0.42 mmol) was dissolved in THF (40 mL), and *tert*-butyl isocyanide (48 μL, 0.42 mmol) was added to the stirred solution. After the reaction mixture was refluxed for 6 h, the colorless solution had turned bright yellow. The solvent was reduced in vacuo to 10% of its volume. Pentane (50 mL) was added, and a solid precipitated, which was filtered off, washed twice with pentane (25 mL), and dried in vacuo. Yield: 350 mg of a bright yellow powder (87%).

B. *tert*-Butyl isocyanide (28 μL, 0.23 mmol) was added to a solution of [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1a**) (198.2 mg, 0.23 mmol) in toluene (50 mL). After the reaction mixture was stirred for 15 min at room temperature, the solvent was concentrated to 10 mL and pentane (30 mL) was added. The bright yellow precipitate was filtered out, washed twice with pentane (15 mL), and dried in vacuo. Yield: 177.5 mg **2a** as a powder (89%). Crystals suitable for X-ray diffraction were grown by slowly distilling hexane into a saturated solution of **2a** in THF at ambient temperature. Anal. Calcd for C$_{46}$H$_{46}$BrNP$_2$Pt: C, 58.17; H, 4.88; N, 1.47; P, 6.52. Found: C, 57.83; H, 4.98; N, 1.51; P, 6.39. FD-mass: found m/z = 950; calcd M$^{\bullet+}$ = m/z 949.8.

***trans*-[PtCl{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2b).** The reaction of [PtCl{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1b**) (304.2 mg, 0.37 mmol) in THF (50 mL) with *tert*-butyl isocyanide (43 μL, 0.37 mmol) yielded 261.9 mg (78%) of **2b** as a bright yellow powder.

***trans*-[PtBr{C(C(-CH$_2$-)$_5$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2c).** The reaction of [PtBr{C(H)=C=C-(CH$_2$)$_5$-}(PPh$_3$)$_2$] (**1c**) (143.5 mg, 0.158 mmol) in THF (75 mL) with *tert*-butyl isocyanide (18 μL, 0.158 mmol) yielded 123 mg (79%) of **2c** as a bright yellow powder. FD-mass: found m/z = 990; calcd M$^{\bullet+}$ = m/z 989.9.

***trans*-[PtBr{C(CMe(Et))(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2d).** The reaction of [PtBr{C(H)=C=CMe(Et)}(PPh$_3$)$_2$] (**1d**) (144.2 mg, 0.164 mmol) in THF (50 mL) with *tert*-butyl isocyanide (19 μL, 0.164 mmol) yielded 127 mg (79%) of **2c** as a bright yellow powder. FD-mass: found m/z = 964; calcd M$^{\bullet+}$ = m/z 963.9.

***trans*-[PtBr{C(CMe$_2$)(CH=C=Nxyl)}(PPh$_3$)$_2$] (2i).** An amount of 1.0 equiv of 2,6-xylyl isocyanide (23.5 mg, 0.18 mmol) was added to a solution of [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1a**) (155.2 mg, 0.18 mmol) in THF (40 mL). After refluxing for 6 h, the colorless solution turned orange-brown. The same procedure as described above afforded 105.8 mg of the yellow **2i** (59% yield). Anal. Calcd for C$_{50}$H$_{46}$BrNP$_2$Pt: C, 60.18; H, 4.65; N, 1.40; P, 6.21. Found: C, 60.27; H, 4.78; N, 1.47; P, 6.19. FD-mass: found m/z = 998; calcd M$^{\bullet+}$ = m/z 997.8.

Attempted Synthesis of [PdBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2j). Reactions of [PdBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1j**) (256.9 mg, 0.33 mmol) with 1 equiv of *tert*-butyl isocyanide (37 μL, 0.33 mmol) were carried out in both THF and benzene (ca. 30 mL). After adding the *tert*-butyl isocyanide at room temperature, the color of the solution turned from yellow to orange immediately and the title compound **2j** was formed instantaneously. Upon evaporation of the solvent, the initially orange reaction mixture gradually darkened and a brown-orange solid was isolated, which gave a poor elemental analysis. When the reaction was carried out in cold THF or toluene (both −70 °C), the palladium compound **2j** could not be isolated in a pure form either.

Synthesis of the Ionic Platinum Complexes 3a–h. The synthesis of *trans*-[Pt{C(H)=C=CMe$_2$}(CN-*t*-Bu)(PPh$_3$)$_2$]Br (**3a**) from the reaction of [PtBr(C(H)=C=CMe$_2$)(PPh$_3$)$_2$] (**1a**) and *tert*-butyl isocyanide is described in detail; the syntheses of **3b–h** were carried out similarly.

***trans*-[Pt{C(H)=C=CMe$_2$}(CN-*t*-Bu)(PPh$_3$)$_2$]Br (3a).** To a colorless solution of [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1a**) (277 mg, 0.32 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature was added *tert*-butylisocyanate (36 μL, 0.32 mmol). After stirring for 2 min, the solvent was reduced in vacuo to 10% of the volume. Subsequently, pentane (20 mL) was added, after which a white solid precipitated. The solid was filtered off, washed with diethyl ether (25 mL) and pentane (2 × 25 mL), and dried in vacuo to give 269 mg of **3a** as a white powder (89% yield). Anal. Calcd for C$_{46}$H$_{46}$BrNP$_2$Pt: C, 58.17; H, 4.88; N, 1.47; P, 6.52. Found: C, 56.71; H, 4.96; N, 1.51; P, 6.31. FD-mass: found m/z = 950; calcd M$^{\bullet+}$ = m/z 949.8.

***trans*-[Pt{C(H)=C=CMe$_2$}(CN-*t*-Bu)(PPh$_3$)$_2$]Cl (3b).** The reaction of [PtCl{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1b**) (99.4 mg, 0.12 mmol) in CH$_2$Cl$_2$ (20 mL) with *tert*-butyl isocyanide (14 μL, 0.12 mmol) yielded 94.2 mg (86%) of **3b** as a white powder. FD-mass: found m/z = 905; calcd M$^{\bullet+}$ = 905.4.

***trans*-[Pt{C(H)=C=C-(CH$_2$)$_5$-}(CN-*t*-Bu)(PPh$_3$)$_2$]Br (3c).** The reaction of [PtBr{C(H)=C=C(c-Hex)}(PPh$_3$)$_2$] (**1c**) (250 mg, 0.28 mmol) in CH$_2$Cl$_2$ (20 mL) with *tert*-butyl isocyanide (32 μL, 0.28 mmol) yielded 249 mg (90%) of **3d** as a white powder. Anal. Calcd for C$_{49}$H$_{50}$BrNP$_2$Pt: C, 59.45; H, 5.09; N, 1.41; P,

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6.26. Found: C, 55.76; H, 5.01; N, 1.56; P, 5.91. FD-mass: found m/z = 990; calcd $M^{\bullet+}$ = m/z 989.9.

***trans*-[Pt{C(H)=C=CMe(Et)}(CN-*t*-Bu)(PPh_3)$_2$]Br (3d).** The reaction of [PtBr{C(H)=C=CMe(Et)}(PPh_3)$_2$] (1d) (105.0 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) with *tert*-butyl isocyanide (14 μL, 0.12 mmol) yielded 93.7 mg (81%) of **2c** as a white powder. Anal. Calcd for $C_{47}H_{48}BrNP_2Pt$: C, 58.57; H, 5.02; N, 1.45; P, 6.43. Found: C, 58.44; H, 4.96; N, 1.49; P, 6.45. FD-mass: found m/z = 964; calcd $M^{\bullet+}$ = m/z 963.9.

***trans*-[Pt{C(H)=C=CMe(*t*-Bu)}(CN-*t*-Bu)(PPh_3)$_2$]Br (3e).** The reaction of [PtBr{C(H)=C=CMe(*t*-Bu)}(PPh_3)$_2$] (1e) (56.8 mg, 0.06 mmol) in CH_2Cl_2 (20 mL) with *tert*-butyl isocyanide (7.2 μL, 0.06 mmol) yielded 45.9 mg (74%) of **3e** as a white powder. FD-mass: found m/z = 992; calcd $M^{\bullet+}$ = m/z 991.9.

***trans*-[Pt{C(H)=C=CMe(*t*-Bu)}(CN-*t*-Bu)(PPh_3)$_2$]I (3f).** The reaction of [PtI{C(H)=C=CMe(*t*-Bu)}(PPh_3)$_2$] (1f) (394.1 mg, 0.41 mmol) in CH_2Cl_2 (40 mL) with *tert*-butyl isocyanide (49.2 μL, 0.41 mmol) yielded 261 mg (61%) of **3f** as a white powder. FD-mass: found m/z = 1039; calcd $M^{\bullet+}$ = m/z 1038.9.

***trans*-[Pt{C(H)=C=CH(*n*-Pe)}(CN-*t*-Bu)(PPh_3)$_2$]Br (3g).** The reaction of [PtBr{C(H)=C=CH(*n*-Pe)}(PPh_3)$_2$] (1g) (246.5 mg, 0.27 mmol) in CH_2Cl_2 (40 mL) with *tert*-butyl isocyanide (31.2 μL, 0.27 mmol) yielded 218 mg (81%) of **3f** as a white powder. FD-mass cation: found m/z = 911; calcd $M^{\bullet+}$ = m/z 911.

***trans*-[Pt{C(H)=C=CH(Ph)}(CN-*t*-Bu)(PPh_3)$_2$]Br (3h).** The reaction of [PtBr{C(H)=C=CH(Ph)}(PPh_3)$_2$] (1h) (269.2 mg, 0.29 mmol) in CH_2Cl_2 (30 mL) with *tert*-butyl isocyanide (33.9 μL, 0.29 mmol) yielded 195.1 mg (66%) of **3f** as a white powder. Anal. Calcd for $C_{50}H_{48}BrNP_2Pt$: C, 60.18; H, 4.65; N, 1.40; P, 6.21. Found: C, 59.79; H, 4.58; N, 1.38; P, 5.98. FD-mass cation: found m/z = 917; calcd $M^{\bullet+}$ = m/z 917.

Monitoring the Reaction of [MX{C(H)=C=CRR′}(PPh_3)$_2$] (1) with *t*-BuNC. NMR Experiments. Solutions for NMR experiments were obtained by dissolving a weighed amount of the reactant in 1.5 mL of degassed deuterated solvent (THF, CD_2Cl_2, or toluene). Part of this solution was transferred to a standard 5-mm NMR tube. The NMR tube was cooled or heated to the desired temperature as required. After a spectrum of the starting compound was taken, 1 equiv *t*-BuNC was added. ^1H and ^{31}P NMR spectra were recorded at regular time and temperature intervals.

FT-IR Experiments. Solutions for FT-IR experiments were obtained by dissolving a weighed amount of the reactant in 4 mL of dry degassed THF. The solution was syringed into the reaction vessel of the FAIR cell. A spectrum of the starting compound was recorded. Subsequently, 1 equiv of *t*-BuNC was added to the reaction chamber. The reaction was, while stirring, followed as a function of time by means of FT-IR spectroscopy.

Crystal Structure Determination of Bis(triphenylphosphine)bromo(2,2,7-trimethyl-3-azaocta-3,4,6-trien-6-yl)platinum(II) [PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh_3)$_2$] (2a). Crystals of **2a** are triclinic, space group $P\bar{1}$, with two formula units $C_{46}H_{46}BrNP_2Pt$ in a unit cell of dimensions a = 11.907(2) Å, b = 12.603 (2) Å, c = 14.862(3) Å, α = 81.74(2)°, β = 78.50(2)°, γ = 72.43(2)°, V = 2075.8(3) Å^3, D_{calcd} = 1.52 g·cm^{-3}, and μ(Mo Kα) = 44.8 cm^{-1}. A total of 12 001 intensities (2.2 ≤ 2θ ≤ 60°; $-16 \le h \le 16$, $-17 \le k \le 17$, $0 \le l \le 20$) were measured on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo Kα radiation at room temperature. Of these, 3108 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved. The dimensions of the crystal were 0.38 × 0.23 × 0.50 mm. The structure was solved using the Patterson method, which yielded the positions of the Pt and Br atoms, and the other non-hydrogen atoms were found by means of subsequent difference Fourier syntheses. The H atoms were calculated and refined isotropically. Refinement proceeded through block-diagonal least-squares calculations, anisotropic for the non-hydrogens atoms, employing a weighting scheme, $w = 1/(5.62 + F_o + 0.0334F_o^2)$. An empirical absorption correction (DIFABS) was used,[5] and an extinction correction was applied. The anomalous dispersion of Pt, Br, and P were taken into account. The final R value was 0.037 for 8893 observed reflections (R_w = 0.069). The programs used were from XRAY76,[6] and the scattering factors[7] were taken from the literature.

Table I. Crystallographic Data for [PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh_3)$_2$] (2a)

formula	$C_{46}H_{46}BrNP_2Pt$
mol wt	949.813
cryst syst	triclinic
space group	$P\bar{1}$
Z	2
a, Å	11.907(2)
b, Å	12.603(2)
c, Å	14.862(3)
α, deg	81.74(2)
β, deg	78.50(2)
γ, deg	72.43(3)
V, Å^3	2075(3)
D_{calcd}, g·cm^{-3}	1.52
$F(000)$, electrons	944
λ (Mo Kα radiation), cm^{-1}	710 69
$\omega/2\theta$	1
2θ, deg	2.2–60.0
data set	$-16 \le h \le 16, -17 \le k \le 17,$ $0 \le l \le 20$
total no. of reflns	12 001
total no. of less-than $2.5\sigma(I)$	3108
no. of obsd reflns	8893
weighting scheme	$w = 1/(5.62 + F_o + 0.0334F_o^2)$
anomalous scattering	Pt, Br, and P
abs corrn	max 1.183, min 0.843
extinction corrn	isotropic
μ(Mo Kα), cm^{-1}	44.8
scan method; temp, °C	θ–2θ; 20
crys dimens, mm^3	0.38 × 0.23 × 0.50
final R_f, R_w	0.037, 0.069
max shift/error	0.37
residual density, e Å^{-3}	max 0.7, min −0.4
extinction factor	0.72(1) × 10^{-6}
hor and vert aperture	3.6 and 4.0
exposure time, h	93.65
ref reflns	1–11 and −2 to +11
max time/refln, deg min^{-1}	4

Results

Synthesis of the Platinum and Palladium Vinylketenimine Complexes (2a–d, 2i, 2j). The reactions of [PtBr{C(H)=C=CRR′}(PPh_3)$_2$] (**1a–d**) with an equimolar amount of *tert*-butyl isocyanide in THF gave, after heating the reaction mixture for 6 h at 60 °C, the new platinum vinylketenimines **2a–d**. No trace of the initially expected intermediate carbaldimino–allene complex [PtBr{C(=NR″)—C(H)=C=CRR′}(PPh_3)$_2$] (5) was observed in the product.

When the same reactions were carried out in a less polar solvent such as toluene, the platinum vinylketenimine complexes **2a–d** were formed in 15 min at room temperature. When the reaction was performed in dichloromethane, no metal vinylketenimine formation took place. The yellow platinum compounds **2a–d** are soluble in benzene, THF, toluene, and dichloromethane, and they can be stored for months without apparent decomposition if kept at 0 °C in an inert atmosphere. Their structures have been determined by ^1H, ^{31}P, and ^{13}C NMR, IR, FD-mass spectroscopy, elemental analyses, and an X-ray single crystal structure determination of compound **2a** (see below).

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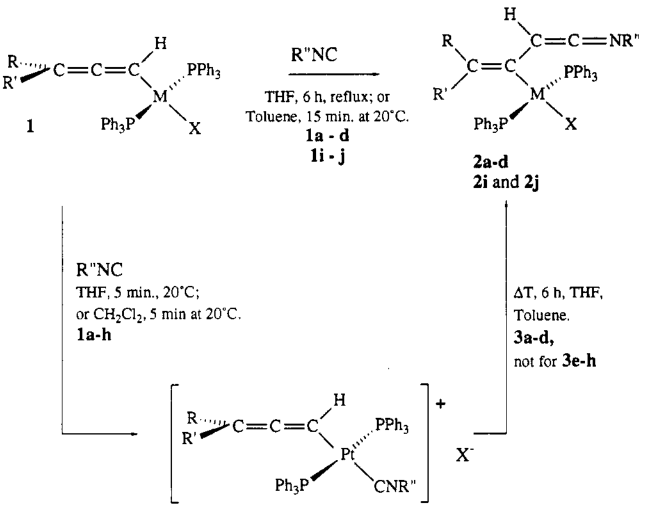
Scheme II. Reactions of Complexes 1 with R″NC[a]



3a-h

[a] M = Pt and R″ = *t*-Bu: (a) R = R′ = Me, X = Br; (b) R = R′ = Me, X = Cl; (c) R–R′ = $-(CH_2)_5-$, X = Br; (d) R = Me, R′ = Et, X = Br; (e) R = *t*-Bu, R′ = Me, X = Br; (f) R = *t*-Bu, R′ = Me, X = I; (g) R = *n*-Pe, R′ = H, X = Br; (h) R = Ph, R′ = H, X = Br. M = Pt and R″ = 2,6-xylyl: (i) R = R′ = Me, X = Br. M = Pd and R″ = *t*-Bu: (j) R = R″ = Me, X = Br.

Reaction of $[PtBr\{C(H){=}C{=}CMe_2\}(PPh_3)_2]$ (**1a**) with xylyl isocyanide in THF at 60 °C for 5 h led to the formation of the platinum *N*-xylylvinylketenimine compound **2i**. This yellow compound shows the same characteristics as **2a–d** and has been fully characterized.

The synthesis of the palladium analogues of **2a–d** was cumbersome. Upon reaction of $[PdBr\{C(H){=}C{=}CMe_2\}(PPh_3)_2]$ (**1j**) with an equimolar amount of *t*-BuNC in THF or benzene at room temperature, the reaction mixture directly turned from yellow to orange, and according to NMR and IR data for the solution, $[PdBr\{(Me_2C)C(CH{=}C{=}N\text{-}t\text{-}Bu)\}(PPh_3)_2]$ (**2j**) was cleanly formed in approximately 5 min, but attempts to isolate **2j** failed. When a solution of **2j** was concentrated (either in vacuo or in a N_2 stream) the orange color turned brown and a brown-orange solid residue could be isolated, of which the elemental analysis was unsatisfactory. In solution the product could be identified as palladium compound **2j**, by ^1H and ^{31}P NMR and IR spectroscopy. The similarity between these data and those of the platinum analogues implies that they have the same structure in solution.

Synthesis of the Ionic Platinum Complexes 3a–h. The syntheses of platinum compounds **2a–d**, in refluxing THF, involved reaction times of 6 h. When instead only short reaction times were employed, viz. 5 min, as well as lower reaction temperatures, or when the reactions were performed in CH_2Cl_2 at 20 °C, instead of either THF or toluene, (σ-allenyl)platinum compounds $[Pt\{C(H){=}C{=}CRR'\}(PPh_3)_2Br]$ (**1a–h**) reacted with 1 equiv of *tert*-butyl isocyanide to yield the ionic compounds **3a–h** in quantitative yields (see Scheme II). These ionic platinum complexes are white solids, which are soluble in dichloromethane and THF and moderately soluble in toluene. They can be handled in air for a short period and can be stored for longer periods in an inert atmosphere at −20 °C.

The pure complexes **3a–d** gave, either gradually after redissolving the complex in THF and refluxing for 6 h or instantly by dissolution in toluene, the platinum vinylketenimine complexes **2a–d**. Interestingly, even after prolonged reaction periods (24 h), complexes **3e–h** could not be converted into the corresponding compounds **2e–h**. Moreover, in boiling CH_2Cl_2 no conversion of **3a–h** into **2a–h** was observed.

Characterization of 2a–d, 2i, and 2j. The identity of the (metallovinyl)ketenimine complexes in solution has been established by ^1H, ^{31}P, and ^{13}C NMR spectroscopy and in the solid state by IR spectroscopy. Selected data have been collected in Tables II and III. The ^{31}P NMR data show for complexes **2a–c**, **2i**, and **2j** a singlet, indicating that the two triphenylphosphine ligands are situated in a mutual trans position. In the platinum complexes $^1J(Pt,P)$ amounts to ca. 3150 Hz, which is a normal value for *trans*-bis(phosphine)platinum complexes.[8] The presence of the ketenimine moiety was indicated by the typical strong asymmetric stretching vibration $\nu(C{=}C{=}N)$ at ca. 2000 cm^{-1} in the IR spectra.

The ^1H NMR spectra of all complexes show two broad multiplets characteristic for ortho and meta/para protons of coordinated triphenylphosphine groups, furthermore a singlet at ca. 1 ppm for the *t*-Bu protons of the N-*t*-Bu group and a singlet at ca. 4.3 ppm for the ketenimine $N{=}C{=}C(H)$ proton ($^3J(Pt,H)$ = ca. 90 Hz) are observed. The (metallovinyl)ketenimine complexes **2a–c**, **2i**, and **2j** show different signals for the R and R′ groups. In these complexes, the groups R and R′ are, due to their spatial disposition (*E* or *Z*) relative to the C=C=N moiety, inherently anisochronic. One of the groups R or R′ exhibits a marked low frequency shift of about 1 ppm as compared to the expected values for the chemical shift in organic vinylketenimines. In metallovinyl complexes, a high frequency shift for the R group in the cis position has frequently been observed.[9] Clearly, the reverse is the case for the presented compounds and the observed low frequency shift of either R or R′ may be explained by invoking the shielding effect of the phenyl groups of the triphenylphosphine ligands. Indeed, from the solid state structure of **2a**, it appears that one methyl group is situated between the phenyl groups of the two triphenylphosphine ligands, whereas the other methyl group is not (see below).

The product from the reaction of $[PtBr\{C(H){=}C{=}CMe(Et)\}(PPh_3)_2]$ (**1d**) with *t*-BuNC showed in the ^{31}P NMR spectrum two singlets, both with platinum satellites. The ^1H NMR spectrum showed a double set of signals for R, R′, the *tert*-butyl group, and the ketenimine proton in a 60/40 ratio, indicating that $[PtBr\{C(C(Me)Et)(CH{=}C{=}N\text{-}t\text{-}Bu)\}(PPh_3)_2]$ (**2d**) exists in two geometrical forms, viz. the *E* and *Z* isomers. The assignment of NMR signals to the two geometric isomers has been effected by invoking the chemical shift dependence on the proximity of the $PtBr(PPh_3)_2$ moiety, as indicated above for the C_s symmetric compounds. The ^1H NMR spectrum of **2j** shows a virtual triplet at 3.88 ppm due to a $^4J(P,H)$ of 4.0 Hz for the ketenimine $N{=}C{=}C(H)$ proton. In the ^1H NMR spectra of **2a–d** and **2i**, however, such a coupling has not been observed. Apparently, the dihedral angle between the metal coordination plane and the ketenimine C—H bond is very close to 90° in the Pt complexes **2a–d**, whereas

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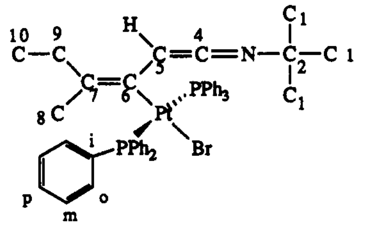
Table II. ^{1}H[a] and ^{31}P[b] NMR and IR[c] Data (*J* in Parentheses) for **2a–d**, **2i**, and **2j**

		^{1}H NMR				^{31}P NMR	IR
compd	solvent	δ(R)	δ(R′)	δ(R″NC)	δ(C—H)[e]	δ(P)[f]	ν(C=C=N)[c]
2a	C_6D_6	0.92 (s)	1.74 (s)	1.00 (s)	4.38 (s, 88)	21.40 (3179)	1995
2b	CD_2Cl_2	0.68 (s)	1.38 (s)	0.99 (s)	4.10 (s, 87)	22.51 (3080)	1997
2c	$CDCl_3$	0.81 (m), 1.04 (m)	2.23 (m), 1.26 (m)	0.98 (s)	4.33 (s, 97)	21.99 (3196)	1993
(*Z*)-2d	$CDCl_3$	0.17 (t), 1.15 (q)	1.56 (m)	1.02 (s)	4.29 (s, 91)	22.98 (3198)	1999
(*E*)-2d	$CDCl_3$	0.64 (m)	2.09 (q), 0.27 (t)	0.98 (s)	4.12 (s, 91)	22.29 (3186)	1999
2i	C_6D_6	1.03 (s)	1.75 (s, 21.1)[e]	2.30 (s), 6.87 (s)	4.36 (s, 90)	20.90 (3159)	2000
2j	C_6D_6	0.95 (s)	1.76 (s)	1.12 (s)	4.10 (t, 4)[d]	21.82	2000

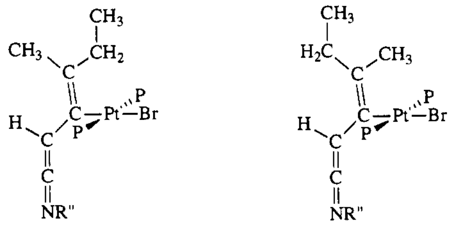
[a] Measured at 300.1 MHz. Multiplicity: s = singlet, m = multiplet, t = triplet, q = quartet. The meta/para and ortho phenyl protons are observed as broad multiplets at δ = 7.0 and 7.4 ppm, respectively. [b] Measured at 120.5 MHz. [c] KBr pellets, in cm^{-1}. [d] *J*(P,H) in Hz. [e] *J*(Pt,H) in Hz. [f] *J*(Pt,P) in Hz.

Table III. ^{13}C{^{1}H} NMR Data for **2a**, **2c**, **2d**, and **2i**[a]



	2a	**2c**	**(*Z*)-2d**	**(*E*)-2d**	**2i**
δ(C_i)[b]	131.47	131.04	131.69	131.69	131.29
δ(C_o)[c]	135.56	135.12	136.01	136.01	135.30
δ(C_m)[d]	127.77	127.24	128.36	128.36	127.70
δ(C_p)	130.48	129.79	130.98	130.98	130.36
δ(C1)	29.94	29.65	30.23	30.29	*f*
δ(C2)	59.47	57.85	59.95	59.15	*f*
δ(C4)	186.59	186.70	186.86	187.49	193.27
δ(C5)	64.97	64.40	65.40	65.94	62.81
δ(C6)[e]	124.66	120.25	125.96	126.91	125.13
δ(C7)	120.94	117.80	122.73	123.33	122.05
δ(C8)	30.22	25.85	17.80	29.85	30.12
δ(C9)	20.22	25.64	37.61	28.80	20.76
δ(C10)		26.39	12.40	11.62	

[a] Measured in $CDCl_3$ at 75.5 MHz, chemical shift in ppm. [b] Virtual triplet ^1J(P,C) of ca. 29 Hz, ^2J(Pt,C) ca. 30 Hz. [c] Virtual triplet ^2J(P,C) ca. 6.8 Hz. [d] Virtual triplet ^3J(P,C) ca. 5.7 Hz. [e] Virtual triplet ^2J(P,C) ca. 5.0 Hz, ^1J(Pt,C) not observed. [f] In compound **2i** R″ = 2,6-xylyl; δ(C_i) = 121.63; δ(C_o) = 139.81; δ(C_m) = 125.26; δ(C_p) = 128.81; δ(C_{Me}) = 19.35.



Z-2d *E*-2d

Figure 2. Two geometric isomers of [PtBr{C(CMeEt)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (**2d**).

it deviates significantly from 90° in the case of the Pd compound **2j**.

The ^{13}C NMR spectra of **2a**, **2c**, **2d**, and **2i** (Table III) are in agreement with the proposed structures. The α-carbon atoms of the ketenimine moiety (C4 in Table III) have been observed at ca. δ = 187 ppm for R″ = *t*-Bu and at δ = 193 ppm for R″ = xylyl, and the β-carbon atoms of the ketenimine moiety (C5 in Table III) resonate at about δ = 65 ppm. These chemical shifts are normal values and are comparable with those observed for noncoordinated ketenimines, i.e. the α-carbon atom at δ = 186–195 and the β-carbon atom at 36–77 ppm.[10] The Pt—*C*=C (C6 in Table III) were observed at approximately δ = 120–125 ppm, and the Pt—C=*C* (C7 in Table III) at δ = 117–123 ppm, which values are in the range observed for the chemical shifts of the comparable carbon atoms in (σ-vinyl)bis(triphenylphosphine)platinum(II) bromides[11] which appear at approximately δ = 126–147 and δ = 115–128 ppm, respectively.

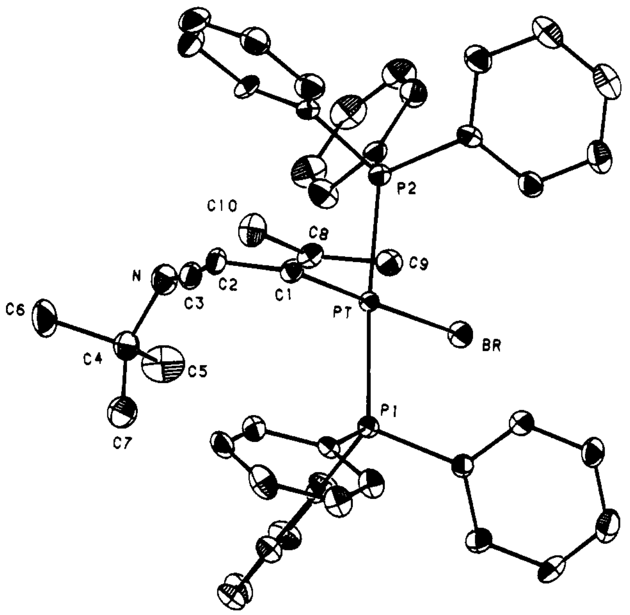


Figure 3. ORTEP drawing of [PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (**2a**).

Solid State Structure of [PtBr{C(CMe$_2$)(CH=C=N-*t*-Bu)}(PPh$_3$)$_2$] (2a). The molecular structure of **2a**, along with the adopted numbering scheme is presented in Figure 3 and selected bond lengths and bond angles are listed in Table IV. The centrosymmetric unit cell contains two enantiomeric (*M* and *P*) four-coordinate Pt monomers. The coordination around platinum can be described as approximately square planar, with the coordination positions around Pt taken by the two phosphorus atoms P1 and P2, in mutual trans positions, by C1 of the vinylketenimine ligand, and by Br. If the least-squares plane through these four atoms is calculated, the phosphorus atoms P1 and P2 both are positioned above this plane, and the bromide and C1 below this plane; hence the coordination geometry is distorted from square planar toward a tetrahedron. The magnitude of this distortion can be expressed by the parameter Δ.[12] For **2a** a value Δ

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Table IV. Relevant Bond Lengths (Å) and Bond Angles (deg) with Esds in Parentheses for 2a

	Around Pt		
Pt–Br	2.5464(9)	Br–Pt–P1	91.23(5)
Pt–P1	2.324(2)	Br–Pt–P2	89.93(5)
Pt–P2	2.312(2)	Br–Pt–C1	176.2(2)
Pt–C1	2.050(6)	P1–Pt–P2	173.40(6)
		P1–Pt–C1	91.6(2)
		P2–Pt–C1	87.5(2)
	Within the Vinyl Ketenimine Ligand		
C1–C2	1.45(1)	Pt–C1–C2	114.6(5)
C1–C8	1.32(1)	Pt–C1–C8	123.2(5)
C2–C3	1.32(1)	C2–C1–C8	122.1(6)
C3–N	1.22(1)	C1–C2–C3	128.3(7)
C4–C5	1.50(2)	C2–C3–N	172(1)
C4–C6	1.54(1)	C5–C4–N	113.9(9)
C4–C7	1.53(2)	C6–C4–N	104.5(9)
C4–N	1.47(1)	C7–C4–N	108(1)
C8–C9	1.50(1)	C3–N–C4	126(1)
C8–C10	1.53(1)	C1–C8–C9	123.7(6)
		C1–C8–C10	123.6(7)
		C9–C8–C10	112.7(7)

= 0.93 has been calculated, which resembles those of other *trans*-PtBr(R)$(PR_3)_2$ structures.[4] The dihedral angle between the planes defined by P1—Pt—Br and P2—Pt—C1 amounts to 26.9° and the nonbonding Pt···C9 distance is 3.3040 Å.

The Pt–P (2.324(2) and 2.312(2) Å) and Pt–Br (2.5464(9) Å) bond distances are normal, when compared to those reported.[13-17] The Pt–C1 bond distance of 2.050(6) Å is as expected for C(sp^2) to Pt bonds[18] and indicates a single bond between Pt and C1. The Pt–C1 bond distance and the Pt–C1–C8 bond angle (1.32(1) Å and 123.2(5)°) may be compared with those in *trans*-bromo((*E*)-styryl)bis(triphenylphosphine)platinum(II),[14] which are 2.022(8) Å and 123.8(6)°, respectively.

The bond distances and electronic structure of a ketenimine are known to depend on the relative contribution of several possible resonance structures[19] (**F–H** in Figure 4). In connection with this the C3-N bond distance and the C3-N-C4 angle merit some discussion. An example of this dependence has been presented by Daly,[20] who found the CN bond length of $(Me_2OS)_2C{=}C{=}NEt$ (1.165 Å) to approach the value of a CN triple bond length, and Wheatley,[21] who observed a similar CN bond length for $(Me_2OS)_2C{=}C{=}NMe$ (1.154 Å). Furthermore, the C—N—C bond angle in $(Me_2OS)_2C{=}C{=}NEt$ is about 145°, whereas this angle in $(Me_2OS)_2C{=}C{=}NMe$ amounts to 180°. The C3—N bond length of 1.22(1) Å of **2a** is short for a CN double bond, but long for a CN triple bond and the C3—N—C4 bond angle of 126(1)° of **2a** is significantly smaller compared to those in $(Me_2OS)_2C{=}C{=}NEt$ and $(Me_2OS)_2C{=}C{=}NMe$. Comparison of the CN bond distance and the C—N—C bond angle of **2a** with those of the free ketenimine molecules indicates that **2a** has less contribution from resonance structure **G** than either $(Me_2OS)_2C{=}C{=}NEt$[20] or $(Me_2OS)_2C{=}C{=}NMe$.[21] So we may conclude that the ketenimine **2a** has a large contribution from structure **F**, which is linear with two orthogonal double bonds and an sp^2 hybridization for both the N and C2 atoms. The ketenimine itself is almost linear with a C2—C3—N bond angle of 172(1)°. Having a large contribution from resonance structure **F** also means that the ketenimine ligand is chiral (resonance structure **G** and **H** are not), and both enantiomers have been observed in the centrosymmetric unit cell.

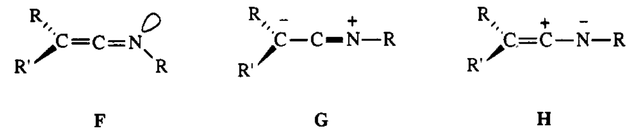

Figure 4. Resonance structures of organic ketenimines.

The atoms C8, C1, C2, C3, and N all lie in a plane, with a maximum deviation of 0.055(9) Å. The angle between this plane and the platinum coordination plane amounts of 81.8(2)°. The C1-C2 bond distance of 1.45(1) Å is normal for a C_{sp^2}-C_{sp^2} distance, and the C2–C3 bond distance of 1.32(1) Å is of the same order of magnitude compared to the same distance in other ketenimines (usualy 1.33 Å).[10]

Characterization of 3a–h. The structure of the ionic complexes **3a–h** in solution has been studied by ^{1}H, ^{31}P, and ^{13}C NMR (Tables V and VI) and FD-mass spectroscopy (see Experimental Section). The structure in the solid state was studied by IR spectroscopy (Table V). The ^{31}P NMR data for compounds **3a–h** all show a singlet at approximately 17.5 ppm with a ^{1}J(Pt,P) of ca. 2750 Hz, consistent with two phosphines in mutual trans positions (cf. similar complexes in ref 23). The appreciable decrease of the ^{1}J(Pt,P) in **3a–h** as compared to that in **1a–h**[4b] can be explained by a decrease of the electron density on platinum in the ionic complexes relative to the neutral complexes, which results in a decreased σ-electron density in the Pt–P bond.[24]

The ^{1}H NMR spectra of **3a–h** show the same characteristics as described for the starting compounds,[4b] except that the coupling constants *J*(Pt,H) are smaller in **3a–h** for the same reasons as described above for the decrease in ^{1}J(Pt,P) in **3a–h**. Furthermore each compound shows a singlet at approximately 0.65 ppm, which is consistent with the presence of a *tert*-butyl group. The ^{13}C NMR spectra (Table VI) show the allenyl carbon atoms at a slightly higher frequency value as compared to those of the starting compounds,[4b] which likewise may be ascribed to the positive charge on the metal. This shift is largest on the carbon atom directly bonded to platinum and becomes negligible for the carbon atoms of the R and R′ groups.

The IR spectra of **3a–h** all show a $\nu(C{\equiv}N)$ frequency at approximately 2200 cm^{-1}, which is characteristic for a σ-coordinated isocyanide ligand[25] and a little higher than that in noncoordinating isocyanides.[26] Furthermore a very weak absorption band at approximately 1920 cm^{-1} has

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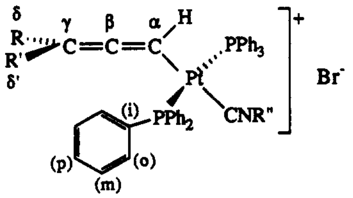
Table V. $^{1}H^{a}$ **and** $^{31}P^{b}$ **NMR and IR**^{c} **Data (*J* in Parentheses) for the Ionic Complexes 3a–h**

	^{1}H NMR			^{31}P NMR	IR	
	δ(R) and δ(R′)	δ(H)^{f}	δ(*t*-Bu)	δ(P)^{b}	ν(CNR″)	ν(C=C=C)
3a	0.78 (d, 3.1,^{d} 15^{e})	5.04 (dt, 100)	0.68 (s)	17.42 (2784)	2200	1930
3b	0.78 (d, 3.1,^{d} 15^{e})	5.03 (dt, 99.9)	0.68 (s)	17.40 (2775)	2200	1925
3c	1.19 (m)	5.11 (dt, 98.9)	0.68 (s)	17.27 (2784)	2210	1920
3d	0.68 (d, 5.8,^{d} CH_3), 1.12 (m, CH_2), 0.44 (t, 7.2,^{g} CH_3)	5.12 (m, 101.6)	0.62 (s)	17.83 (2786)	2200	1922
3e	0.52 (d, 3.3,^{d} CH_3), 0.50	5.27 (m, 99.0)	0.61 (s)	17.46 (2796)	2210	1910
3f	0.60 (d, 2.9,^{d} 14^{e}), 0.52	5.26 (m, 90.2)	0.59 (s)	17.47 (2801)	2210	1910
3g	3.14 (m, 31,^{e} H), 0.78 (t, 7.1,^{g} CH_3), 1.11 (m), 1.29 (m), 1.31 (m)	5.05 (m, 97.1)	0.66 (s)	17.83 (2739)	2210	1920
3h	4.13 (m, 32.1^{e}), 6.33, 6.85	5.62 (m, 117)	0.63 (s)	17.65 (2685)	2195	1904

[a] Measured at 100 and 300 MHz at 25 °C, solvent $CDCl_3$; d = doublet, t = triplet, m = multiplet. The phenyl protons are observed as a broad multiplet at δ = 7.5 ppm. [b] Measured at 40.5 or 121.5 MHz at room temperature; chemical shifts in ppm relative to 85% H_3PO_4, ^{1}J(Pt,P) in Hz; solvent $CDCl_3$. [c] ν in cm^{-1}, KBr pellets. [d] ^{5}J(H,H). [e] *J*(Pt,H) or ^{4}J(Pt,H). [f] ^{2}J(Pt,H). [g] ^{3}J(H,H).

Table VI. $^{13}C\{^{1}H\}$ **NMR Data for 3a, 3b–3e, 3g, and 3h**^{a}



	3a	3c	3d	3e	3g	3h
$\delta(C_i)^{b}$	128.73	128.56	128.56	128.42	128.29	128.12
$\delta(C_o)^{c}$	134.31	134.19	134.35	134.43	134.16	134.13
$\delta(C_m)^{d}$	129.01	128.90	129.03	129.07	128.92	128.98
$\delta(C_p)$	131.87	131.75	131.96	131.97	131.76	131.88
$\delta(C_\alpha)$	86.78	81.30	81.55	83.96	84.21	86.24
$\delta(C_\beta)^{e}$	201.80	198.07	201.19	200.69	202.92	202.60
$\delta(C_\gamma)$	89.50	96.69	95.31	103.02	107.93	88.05
$\delta(C_\delta)$	18.56	29.29	15.95	13.83	27.31	135.54
$\delta(C_{\delta'})$		26.97	26.21	33.86	29.56	127.76
		25.74	12.66	28.81	31.10	125.06
					22.20	125.68
					13.87	
$\delta(\mathit{C}(CH_3)_3)$	58.93	58.76	58.80	58.75	58.85	59.09
$\delta(C(\mathit{C}H_3)_3)$	28.73	28.70	28.65	28.48	28.59	28.55

[a] Measured in $CDCl_3$ at 75.5 MHz, chemical shift in ppm. [b] Virtual triplet ^{1}J(P,C) of ca. 29 Hz, ^{2}J(Pt,C) ca. 30 Hz. [c] Virtual triplet ^{2}J(P,C) ca. 5.6 Hz. [d] Virtual triplet ^{3}J(P,C) ca. 5.2 Hz. [e] Virtual triplet ^{3}J(P,C) between 2.3 and 4.1 Hz.

been observed which can be ascribed to the asymmetric allenyl stretching mode.

In order to obtain further support for the proposed ionic structure of **3a–h**, conductivity measurements of **3a** have been carried out. It appeared that the Λ_m of **3a** in dichloromethane at ambient temperature amounted to 58.8 Ω^{-1} cm^{2} mol^{-1}, which is comparable to that of other 1:1 electrolytes in 1,2-dichloroethane.[27] The molar conductivity of dichloromethane solutions of **1a** and **2a** at room temperature amounted to 0.3 and 0.4 Ω^{-1} cm^{2} mol^{-1}, respectively, which supports their formulation as neutral complexes.

Reactions of 1 with Excess *t*-BuNC. According to ^{31}P NMR spectroscopy, reactions of **1a** with excess *tert*-butyl isocyanide in either THF (60 °C) or toluene (20 °C) resulted in the formation of a mixture of products. The IR spectra of these mixtures show absorptions at 2206 cm^{-1} (assigned to Pt—C≡N—R), 2112 cm^{-1} (free C≡N—R), and 1990 cm^{-1} (assigned to C=C=N). This indicates formation of complexes of the type $[Pt\{C(CRR')(CH{=}C{=}N\text{-}t\text{-}Bu)\}(C{\equiv}N{-}R)(PPh_3)_2]Br$ (See Figure 5). Likewise, when **1e–1h** (or **3e–3h**) are refluxed in the presence of more than 1 equiv of *tert*-butyl isocyanide in THF, mixtures of products are obtained, besides **3e–3h**. The IR spectra of these mixtures show four isocyanide absorptions: 2210 cm^{-1} (Pt—C≡N—R), 2112 cm^{-1} (free C≡N—R), 1990 cm^{-1} (C=C=N), 1640 cm^{-1} (-C(=NR)-). The separation of organoplatinum compounds from this mixture appeared to be impossible, so no elemental analyses could be obtained.

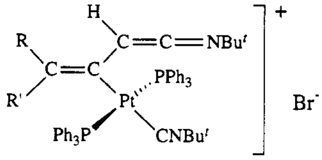


Figure 5. Proposed structure for the product from the reaction of $[PtBr\{C(H){=}C{=}CRR'\}(PPh_3)_2]$ (**1**) with an excess of *t*-BuNC.

In Situ Monitoring of the Reaction of 1a–d with *t*-BuNC, by NMR and IR Spectroscopy. In order to observe possible intermediates in the reactions of **1a–d** with *t*-BuNC, these reactions were monitored by using ^{1}H and ^{31}P NMR as well as IR spectroscopy. When the reaction of **1a** with *tert*-butyl isocyanide was performed in toluene-d_8, the formation of **2a** was complete in ca. 15 min at room temperature. Neither an ionic compound nor any other intermediate could be observed. Monitoring the reaction of **1a** with *tert*-butyl isocyanide in THF-d_8 at −60 °C by ^{1}H NMR spectroscopy, however, revealed the formation of the ionic complex **3a** immediately after the isocyanide had been added. Conversion of **3a** into **2a** could be effected in 17 h by heating the reaction mixture at 30 °C. Formation of complex **3a** was also observed in CD_2Cl_2 at 30 °C, but in this solvent the ionic complex did not react further. Even after heating the dichloromethane solution in a sealed NMR tube for 10 h at 80 °C, no formation of **2a** was observed. Separate IR experiments confirmed the observations made by the NMR experiments, and no other intermediates could be observed.

Similarly, the formation of $[PtCl\{C(CMe_2)(CH{=}C{=}N\text{-}t\text{-}Bu)\}(PPh_3)_2]$ (**2b**) from $[PtCl\{C(H){=}C{=}CMe_2\}(PPh_3)_2]$ (**1b**) and *tert*-butyl isocyanide has been followed by ^{1}H and ^{31}P NMR. In THF-d_8, the reaction was somewhat more sluggish, as it was complete only after 20 h at 40 °C. So, the bromide complex **1a** reacts faster with *t*-BuNC than the chloride complex **1b**, which has been corroborated by showing that in the reaction of a mixture of **1a** and **1b** with *t*-BuNC (in a ratio 1:1:2) in THF first the formation of **2a** was observed and only after some time that of **2b**.

Monitoring the conversions of **1c** and **1d** into **2c** and **2d**, respectively, by means of ^{1}H and ^{31}P NMR and IR spectroscopy, showed the same phenomena as described for **1a** into **2a**.

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Discussion

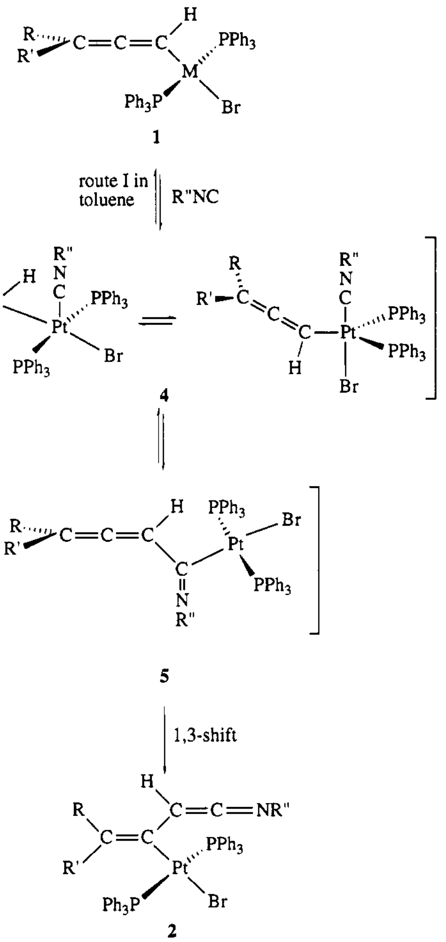
Ketenimines were reported for the first time by Staudinger in 1921,[28] but in the seventies much more information about this type of compounds was accumulated.[29] The first metal complex containing a ketenimine ligand, reported in 1963,[30] is an iron complex with a π-bonded ketenimine. The coordination to a metal fragment can take place in several ways: via the C=C or C=N π-bond (side on) or, as was discovered later,[31] via the nitrogen lone pair (end on). Also in recent years ketenimines appear to be of interest.[32] The preparation of ketenimine metal complexes frequently involves C—C coupling reactions within the ligand sphere of transition metals, e.g. by reacting carbene or carbyne complexes with isocyanides.[33] The (metallovinyl)ketenimine complexes presented here were also formed by a C—C coupling reaction, i.e. of an allene fragment and an isocyanide assisted by the metal, as will be discussed below.

The new organometallic species presented here contain a σ-bonded vinylketenimine. Since the ketenimine is not directly bonded to the metal, its properties can best be compared with *N-tert*-butylketenimines. Indeed, the recently prepared conjugated vinylketenimine $H_2C{=}C(H){-}C(H){=}C{=}N$-*t*-Bu[34] shows spectroscopic features which are very similar to the (metallovinyl)ketenimine reported here.

Mechanistic Aspects. Several mechanisms have been proposed for the insertion of isocyanides into the metal–carbon bond of square planar complexes.[23,35,36] In general, coordination of the isocyanide to the metal prior to displacement of the halide ion is assumed to take place, followed by insertion of the coordinated isocyanide into the M–C bond, possibly through migration of the alkyl or aryl group. Treichel[23] found the rate of insertion to be dependent on the halide atom (I > Br > Cl), which was explained by assuming a nucleophilic attack of the halide ion on the ionic four-coordinated complex as the initial step for insertion. Otsuka *et al.*,[36] however, observed that the insertion rate depends on the steric and electronic effects of the isocyanide used.

The results presented in this paper show for the first time that isocyanide insertion reactions are solvent dependent (see Schemes III and IV). In an apolar solvent such as toluene instant formation of the new platinum vinylketenimine complexes **2a–d** occurs. We proposed that the isocyanide reacts via an intimate (I_A) or associative (A) type of mechanism[37] with the starting allenyl compounds **1**. A five-coordinate intermediate platinum complex **4** is formed, after which a migratory insertion reaction occurs, resulting in the rapid formation of the intermediate allenylimine complex **5**. Subsequently, a 1,3-metal shift occurs with formation of the platinum vinylketenimine complex **2** (route I). Such 1,3-shifts have been documented[38] and play a crucial role in the formation of 2(3*H*)-furanon-5-ylplatinum(II) compounds from (σ-allenyl)platinum complexes by successive CO insertion reactions.[2]

Scheme III. Possible Mechanism of R″NC Insertion into the Pt–C Bond of σ-Allenyl–Pt(II) Complexes in an Apolar Solvent



In the polar noncoordinating solvent CH_2Cl_2, the σ-allenyl compounds **1** react with 1 equiv of isocyanide, forming the ionic species **3** as isolable compounds (Scheme IV, route II), which apparently are kinetically and thermodynamically the most favorable products in this solvent, because even heating at 80 °C in a sealed NMR tube did not result in the expected conversion to the neutral compounds **2**.

In a polar and coordinating solvent like THF, the σ-allenyl compounds **1** react with 1 equiv of isocyanide at room temperature, forming the ionic species **3** (stabilized

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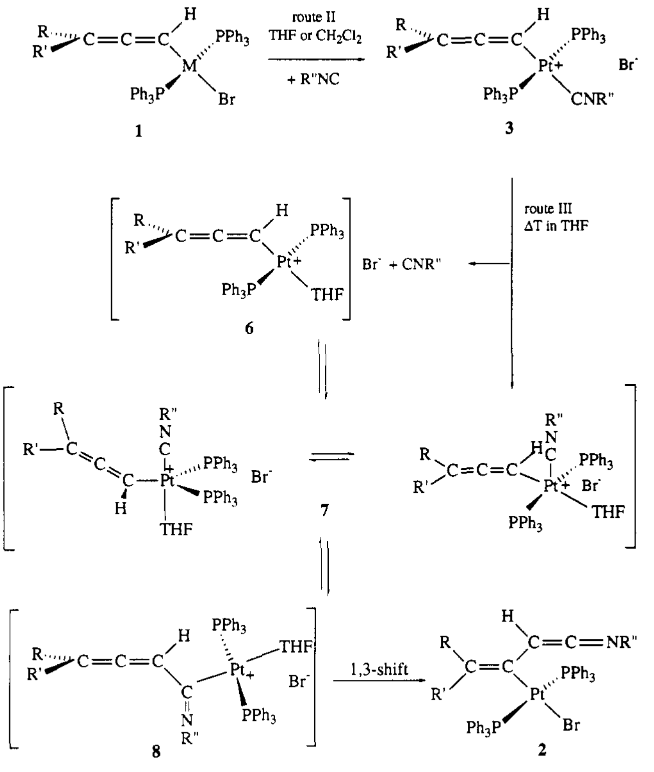
Scheme IV. Possible Mechanism of R″NC Insertion into the Pt–C Bond of σ-Allenyl–Pt(II) Complexes in a Polar Solvent (Route II) and in a Polar Coordinating Solvent (Route III)



by solvatation by THF) (route III). No direct migration insertion can occur in complex **3**, as the allenyl ligand and the isocyanide are situated in a mutual trans position. When species **3** is refluxed in THF, a solvent molecule can create and occupy a fifth coordination site, thus forming complexes like **6** or directly complexes **7** (route III).

Subsequently, migratory insertion of the allenyl ligand from the five-coordinate platinum complex **7**, where the isocyanide is in a cis position to the migrating group, results in the formation of the allenylimine complex **8**, which is then converted into the thermodynamically more stable vinylketenimine complex **2** by a 1,3-metal shift and recoordination of the halide.

In general our mechanistic proposals agree with those suggested before,[23,35,36] since we also propose a five-coordinated transition state, i.e. coordination of the isocyanide upon displacement of the halide in polar solvents, but direct insertion most likely occurs in apolar solvents. In accordance with Treichel's findings,[23] we observed a difference in the rate of insertion for bromide and chloride complexes, respectively, in polar solvents. In addition to Treichel's suggestion that this may be caused by the dependence of the nucleophilicity of the anion on the initial insertion reaction, it could also be due to the dependence on the halide of the termination of the insertion reaction, since in polar solvents the insertion reaction takes place with cationic species to which the halide has to coordinate again after insertion. It is not well understood by compounds **1e–h** in the reaction with isocyanides do not give migratory insertion products, but form the species **3e–h** only. A possibility could be that the large R and R′ groups of **1e–h** on the one hand and the large *tert*-butyl group of the isocyanide on the other experience mutually too much steric hindrance during the conversion of **7** into **8**, which renders this migratory insertion unfavorable. This, however, is in contradiction with the results obtained from the reactions where excess *t*-BuNC has been used. Although we were unable to isolate the products in this case, we may conclude from the IR data that a migratory insertion did occur. Apparently, for insertion in species containing large R and R′ groups, excess nucleophile is necessary to yield migratory insertion products. The fact that excess isocyanide assists in a migratory insertion reaction has already been observed for reactions of $[PdCl(R)(PR'_3)_2]$ with isocyanides.[39]

The insertion reactions of isocyanides and carbon monoxide in (σ-allenyl)platinum(II) systems show resemblances but also differences, the major difference being that isocyanide insertions in these systems are solvent dependent, whereas carbon monoxide insertions in (σ-allenyl)platinum(II) complexes are not.[2] Furthermore, reactions of (σ-allenyl)platinum(II) complexes with CO gave two successive insertions, whereas the corresponding reaction of (σ-allenyl)platinum(II) complexes with R″NC stopped after a single insertion. The resemblance between the two reactions, however, is the occurrence of a structurally analogous intermediate, i.e. platinum vinylketene complex **C** in the CO insertion reactions and the platinum vinylketenimine compounds **2** presented here. This indicates that, for the presented study on insertion reactions involving (σ-allenyl)metal compounds, reactions of isocyanide are a good model for reactions with carbon monoxide.

Note Added in Proof. Relevant recent studies involving π-allenyl complexes are as follows: Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170.

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Supplementary Material Available: A PLUTO drawing of **2a** and tables of fractional coordinates, all bond lengths and angles, and anisotropic thermal parameters of the non-H atoms (10 pages). Ordering information is given on any current masthead page.

OM9301290

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