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Reactions of Acetylenes with Noble Metal Carbonyl Halides. 9.[1] Preparation, Chemical Characterization, and X-ray Structural Analysis of $[\overline{\mathrm{Pt}\{-\mathrm{C}(=\mathrm{O})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{Cl}}\}\mathrm{Cl}]_2$ and the Cyclocarbene Derivative $[\mathrm{Pt}\{\overline{\mathrm{CC}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{O}}\}(\mathrm{PBu}_3)_2\mathrm{Cl}][\mathrm{PF}_6]$

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The cyclopentadienone compound $[\mathrm{Pt}\{\eta^4\text{-}\overline{\mathrm{C}(=\mathrm{O})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})}\}\mathrm{Cl}_2]$ (**1a**) and the octadienoyl complex $[\overline{\mathrm{Pt}\{-\mathrm{C}(=\mathrm{O})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{Cl}}\}\mathrm{Cl}]_2$ (**2a**) were isolated during the reaction of $\mathrm{Pt(CO)_2Cl_2}$ with 4-octyne. The reactions of compounds **1a** and **2a** with nitrogen and phosphorus ligands have also been studied. Compound **2a** reacts with excess of phosphines to give the complex $[\mathrm{Pt}\{\overline{\mathrm{CC}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\text{-}\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{O}}\}\mathrm{L_2Cl_2}]$ [L = $\mathrm{PPh_3}$ (**8a**), $\mathrm{PBu_3}$ (**9a**)], containing a six-membered carbenic ring bonded to platinum, which is easily transformed into the ionic $[\mathrm{Pt}\{\overline{\mathrm{CC}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{C}(\mathrm{Pr})=\mathrm{C}(\mathrm{Pr})\mathrm{O}}\}(\mathrm{PBu}_3)_2\mathrm{Cl}][\mathrm{PF}_6]$ complex (**11a**). The analogous products obtained in the reaction of 2-butyne and 3-hexyne with $\mathrm{Pt(CO)_2Cl_2}$ have been reformulated. A ^{13}C NMR study on a series of derivatives is reported. The crystal structures of complexes **2a** and **11a** have been determined by X-ray diffraction. Crystals of **2a** are triclinic of space group $P\bar{1}$ with $Z = 1$, $a = 8.256$ (2) Å, $b = 10.293$ (3) Å, $c = 12.632$ (3) Å, $\alpha = 73.50$ (2)°, $\beta = 76.50$ (1)°, and $\gamma = 81.62$ (2)°. A total of 2762 reflections were used in the refinement, resulting in a final R of 0.034. The dimeric compound **2a** lies on a crystallographic inversion center; the coordination around each platinum is distorted square-planar, with the olefinic double bond approximately perpendicular to the coordination plane. Crystals of **11a** are orthorhombic of space group $P2_12_12_1$ with $Z = 4$, $a = 25.394$ (6) Å, $b = 14.897$ (4) Å, and $c = 13.858$ (3) Å. The final agreement factor is $R = 0.057$ for 2198 independent observed reflections. The coordination around platinum is, as expected, square-planar with a Pt–C distance of 1.94 (2) Å.

Introduction

It has been found that several metal carbonyl complexes react with substituted alkynes to produce organic compounds containing both carbon monoxide and alkyne-derived fragments; organometallic complexes containing σ- and/or π-bonded cyclic organic systems derived from alkyne fragments with insertion of carbon monoxide groups are also formed.[2] The reaction conditions, such as solvents and temperature, play an important role in determining the nature and yields of the products. Moreover, the nature of the products varies considerably when both the alkyne and the metal complex are changed. These reactions, which have been extensively studied in the case of $\mathrm{Fe_3(CO)_{12}}$,[3] $\mathrm{Fe(CO)_5}$,[3] and $\mathrm{Pd(NCC_6H_5)_2Cl}$, under carbon monoxide atmosphere,[4] yield cyclopentadienone and quinone derivatives together with a large variety of complexes.

We have already fully characterized the reaction of $\mathrm{Pt(CO)_2Cl_2}$ with ethyl phenylpropiolate, resulting in the dimerization of the alkyne with carbonyl insertion and the formation of a cyclocarbene complex.[5] Dialkylacetylenes such as R–C≡C–R (R = Me,[6,7] Et,[6,7] Pr[7]) react with $\mathrm{Pt(CO)_2Cl_2}$ to form, as the main product, the cationic tetrasubstituted cyclobutadiene complex $\mathrm{[Pt_2(C_4R_4)_2Cl_3][Pt(CO)Cl_3]}$ and also, in low yields, two different metalloorganic compounds: the yellow **1a** and the white **2a** complexes with the identical molecular formula $\mathrm{[Pt(C_2R_2)_2(CO)Cl_2]}$. The reactivity and the spectroscopic data of these latter two compounds so far did not permit an unambiguous characterization. Therefore, we decided to reexamine these products in order to clarify how the organic ligands are bonded to the metal atom.

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[2] See, for example: Hubel, W. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. I, p 273. Bowden, F. L.; Lever, A. B. P. *Organomet. Chem. Rev.* **1968**, *3*, 227. Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

[3] Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallics Compounds*; Methuen: London, 1968; Vols. 1 and 2, p 288.

[4] Kelley, E. A.; Wright, G. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 178 and references therein.

[5] Canziani, F.; Galimberti, F.; Garlaschelli, L.; Malatesta, M. C.; Albinati, A.; Ganazzoli, F. *J. Chem. Soc., Dalton Trans* **1983**, 827.

[6] Canziani, F.; Malatesta, M. C. *J. Organomet. Chem.* **1975**, *90*, 235.

[7] Canziani, F.; Galimberti, F.; Garlaschelli, L.; Malatesta, M. C.; Albinati, A. *Gazz. Chim. Ital.* **1982**, *112*, 323.

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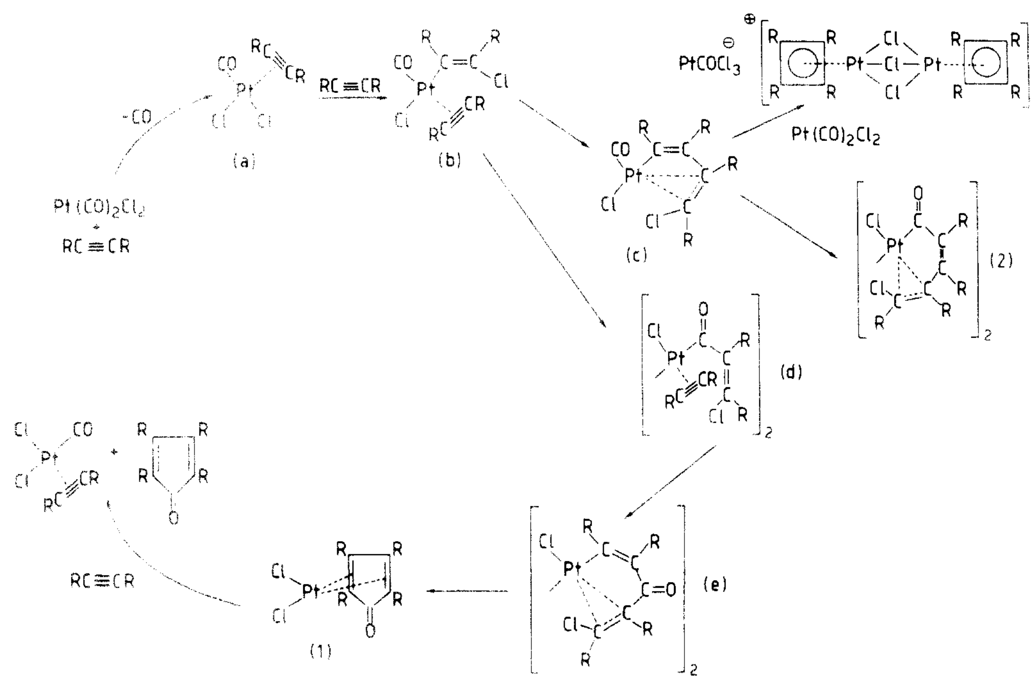
Scheme I. A Possible Pathway for the Reaction of $Pt(CO)_2Cl_2$ with 4-Octyne ($R = C_3H_7$)



In this paper we report the results of such investigation. Compound **1a** is a tetrasubstituted cyclopentadienone platinum(II) complex; for **2a** an X-ray crystal determination clarified the bonding and geometry of the compound, showing a cyclometalated octadienoyl complex of platinum(II), with one of the double bonds π coordinated to the platinum atom to give an almost strain-free "five and a half"-membered ring.[8]

Compound **2a** reacts with phosphorus-containing ligands, and structural modifications of the organic fragment are evident from the ^{13}C NMR spectra. An X-ray structure determination of one of these derivatives (complex **11a**) showed the formation of a cyclocarbene complex, and the ^{13}C NMR spectra allowed us to establish a unique relationship between this compound and its precursors.

Results and Discussion

$Pt(CO)_2Cl_2$ reacts rapidly, in toluene, at room temperature with 4-octyne (molar ratio of $Pt(CO)_2Cl_2$ to 4-octyne = 1:4), to produce a mixture containing $[Pt_2(C_2Pr_2)_4Cl_3][Pt(CO)Cl_3]$ and **1a** and **2a** derivatives. In heptane the reaction is slow but particularly convenient for the separation and purification of compounds **1a** and **2a**, due to the minor degree of polymerization of 4-octyne to give organic products. The yields of pure products **1a** and **2a** are low, but the overall yield, based on platinum, is 90%.

In scheme I, a possible pathway for the reaction of $Pt(CO)_2Cl_2$ with 4-octyne is reported, showing the formation of $[Pt_2(C_2Pr_2)_4Cl_3][Pt(CO)Cl_3]$[7] and of compounds **1a** and **2a**.[9]

These compounds analyzed as $Pt(C_2Pr_2)_2(CO)Cl_2$ with the parent peak in the mass spectra occurring at m/e 514, in agreement with the molecular formula. However, a different fragmentation pattern and other spectroscopic data suggest that the two compounds contain different organic ligands. For instance, the IR spectrum (Nujol mull) of the yellow complex **1a** shows a strong absorption band at 1711 cm^{-1}, while the white compound **2a** shows a strong absorption band at 1682 cm^{-1} and a weak one at 1638 cm^{-1}, due to the stretching of the carbonyl group.

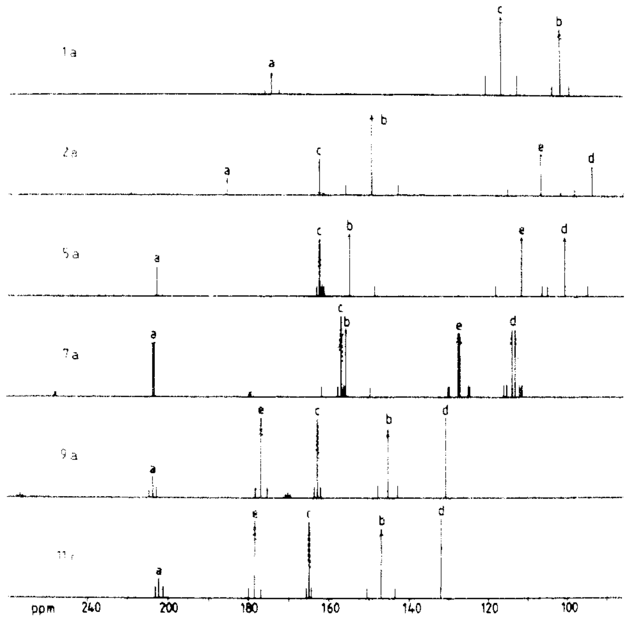


Figure 1. ^{13}C NMR schematic spectra.

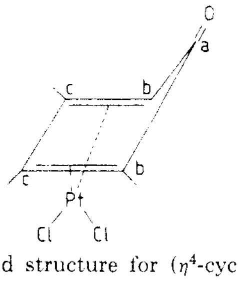


Figure 2. Proposed structure for (η^4-cyclopentadienone)dichloroplatinum.

Chemical Characterization of 1a. Compound **1a** is stable in the air for prolonged period of time and very soluble in acetone, CH_2Cl_2, $CHCl_3$, and toluene. The IR spectrum shows, in the low stretching region, two bands at 343 (w) and 333 (sh) cm^{-1} due to the presence of the two chlorine atoms in a cis configuration around platinum. The

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(8) Omae, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 889.

(9) The lower case letters a, b, and c, prefaced by a number, indicate the 4-octyne, the 2-butyne, and the 3-hexyne derivatives, respectively.

Table I. Carbon-13 NMR Spectral Data[a] (in the Range 80–250 ppm)[10]

	C(a)	C(b)	C(c)	C(d)	C(e)
[Pt[η^4-(C^a(=O)C^b(Pr)=C^c(Pr)C^c(Pr)=C^b(Pr)]-Cl_2] (**1a**)	172.7 ($^2J_{Pt\text{-}C}$ = 79)	100.9 ($^1J_{Pt\text{-}C}$ = 93)	115.9 ($^1J_{Pt\text{-}C}$ = 160)		
[Pt{–C^a(=O)C^b(Pr)=C^c(Pr)C^d(Pr)=C^e(Pr)Cl}-$Cl]_2$[b] (**2a**)	184.6 ($^1J_{Pt\text{-}C}$ = 972)	148.6 ($^2J_{Pt\text{-}C}$ = 263)	162.4[d]	93.7 ($^1J_{Pt\text{-}C}$ = 337)	106.1 ($^1J_{Pt\text{-}C}$ = 349)
[Pt{–C^a(=O)C^b(Pr)=C^c(Pr)C^c(Pr)C^d(Pr=C^e-(Pr)Cl}($C_5H_{11}N$)Cl] (**5a**)	201.7[c]	150.4 ($^2J_{Pt\text{-}C}$ = 252)	161.6 ($^3J_{Pt\text{-}C}$ = 29)	100.3 ($^1J_{Pt\text{-}C}$ =233)	110.8 ($^1J_{Pt\text{-}C}$ = 268)
[Pt{–C^a(=O)C^b(Pr)=C^c(Pr)C^d(Pr)=C^e(Pr)Cl}-(PBu_3)Cl] (**7a**)	202.9 ($^1J_{Pt\text{-}C}$ = 933, $^2J_{P\text{-}C}$ = 3)	154.7 ($^2J_{Pt\text{-}C}$ = 245, $^3J_{P\text{-}C}$ = 1)	156.5 ($^2J_{Pt\text{-}C}$ = 27)	113.2 ($^1J_{Pt\text{-}C}$ = 76, $^2J_{P\text{-}C}$ = 21)	126.6 ($^1J_{Pt\text{-}C}$ = 196, $^2J_{P\text{-}C}$ = 4)
[Pt{C^aC^b(Pr)=C^c(Pr)C^d(Pr)=C^e(Pr)O}-$(PBu_3)_2Cl_2$] (**9a**)	202.7 ($^1J_{Pt\text{-}C}$ = 1349, $^2J_{P\text{-}C}$ = 9)	144.5 ($^2J_{Pt\text{-}C}$ = 93)	162.2 ($^3J_{Pt\text{-}C}$ = 29.4)	129.8	176.2 ($^3J_{Pt\text{-}C}$ = 55)
[Pt{C^aC^b(Et)=C^c(Et)C^d(Et)=C^e(Et)O}-$(PBu_3)_2$Cl][PF_6] (**11c**)	201.6[c]	145.7 ($^2J_{Pt\text{-}C}$ = 95)	164.1 ($^3J_{Pt\text{-}C}$ = 26)	131.3	177.7 ($^3J_{Pt\text{-}C}$ = 55)

[a] a, b, c, d, and e label a specific carbon atom; $CDCl_3$ solution; chemical shifts in ppm; coupling constant in Hz. [b] CH_2 resonances at δ 42.34, 34.05, 31.46, 28.03, 22.19, 22.04, and 21.17 (× 2); CH_3 resonances at δ 14.84, 14.23, 14.09, and 13.94. [c] Broad signal, $^1J_{Pt\text{-}C}$ not detected. [d] Broad, poor resolution of this signal.

^1H NMR spectrum ($CDCl_3$) has a complicate set of signals, consistent with the presence of two nonequivalent propyl groups. In the ^{13}C NMR spectrum of compound **1a** (see Table I and Figure 1)[10] three signals are present in the region 80–250 ppm. These observations and the analytical data can be rationalized in terms of a cyclopentadienone ligand bonded to platinum, as shown in Figure 2. The Pt–C coupling constants for carbons C(b) and C(c) are markedly different, suggesting that the Pt–C(c) distance is shorter than that between Pt and C(b), in agreement with structural data obtained for the tricarbonyltetrakis(trifluoromethyl)(cyclopentadienone)iron.[11]

When compound **1a** is reacted with *p*-toluidine in toluene solution at room temperature, the yellow adduct [Pt{η^4-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)}(*p*-$CH_3C_6H_4$-NH_2)Cl_2] (**3a**) was isolated and characterized by elemental analysis. In contrast, the analogous reaction carried out with PPh_3 (molar ratio of **1a** to PPh_3 = 1:1) gives the well-known $Pt(PPh_3)_2Cl_2$ complex, free tetrapropylcyclopentadienone, and unreacted compound **1a**. With use of the stoichiometric amount of PPh_3 (molar ratio of **1a** to PPh_3 = 1:2), $Pt(PPh_3)_2Cl_2$ and the organic tetrapropylcyclopentadienone were obtained quantitatively. The organic compound is unstable under the experimental conditions and slowly dimerizes to the corresponding Diels–Alder derivative, which was identified through mass spectra and comparison with the spectroscopic and analytical data of the analogous compound obtained from $Pt(CO)_2Cl_2$ and 2-butyne (vide infra).

Chemical Characterization of 2a. The white compound **2a** is stable in the air, soluble in CH_2Cl_2, $CHCl_3$, and toluene, sparingly soluble in acetone, and insoluble in MeOH, 2-propanol, and heptane. The IR spectrum (Nujol mull) shows, in the low stretching region, bands at 290 (w) and 275 (sh) cm^{-1} due to the Pt(μ-Cl) bridging deformations, suggesting the presence of dimeric species in the solid state. The molecular weight, obtained by vapor pressure measurements, confirmed that the same situation persists in solution. The ^{13}C NMR spectrum of compound **2a**, reported in Table I and Figure 1, shows five signals in the range δ 80–250 (see below for discussion). Analytical and spectroscopic data are in agreement with an organic fragment derived by dimerization of acetylene and insertion of a carbon monoxide group. The asymmetry of the organic ligand and the complicated bond situation shown in the ^{13}C NMR spectrum has been confirmed and clarified by a single-crystal X-ray structural analysis.

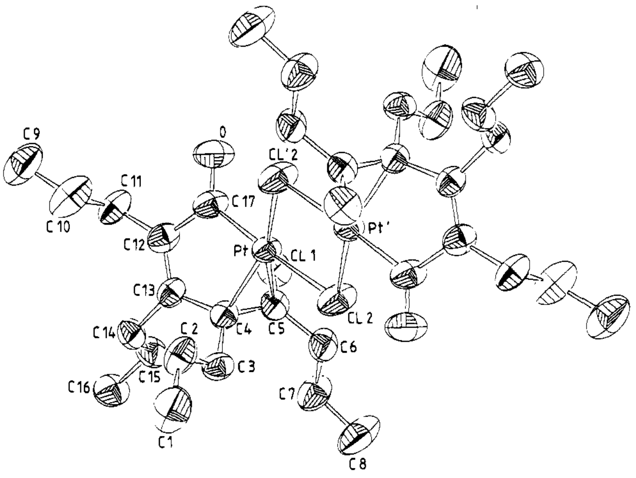

Figure 3. Molecular structure and atom-labeling scheme for [Pt{–C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl}Cl]$_2$ (2a).

Molecular Structure of [Pt{–C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl}Cl]$_2$ (2a) (Chemical Abstracts index name: di-μ-chlorobis[(1,4,5-η)-5-chloro-2,3,4-tripropyl-2,4-octadienoyl]diplatinum). An ORTEP view and the atom-labeling scheme for compound **2a** are given in Figure 3, and the relevant bond lengths and angles are reported in Table II.

The molecule is dimeric and lies on a crystallographic inversion center so that only half of the molecule is independent. The platinum atom shows a distorted square-planar coordination with the two bridging chlorine atoms Cl(2) and Cl′(2) trans to the σ-bonded acyl carbon atom C(17) and to the coordinated olefinic bond, respectively. Therefore the acyl-metalated ring is both σ- and π-bonded to the platinum atom and may be defined as composed of n + 0.5 (n = 5) members.[8] The distance Pt–C_m (C_m being the midpoint of the double bond) is 1.986 (7) Å. Both Pt–C separations of the olefinic carbon atoms (average value 2.108 (8) Å) and the angles Pt–C_m–C(4) and Pt–C_m–C(5) (average value 90.0 (4)°) are equal, showing that the olefinic moiety is symmetrically bonded to platinum. The Pt–C distances are comparable to those observed in the case of Zeise's salt (average values: 2.13 (2) Å for the X-ray determination and 2.131 (3) Å for the neutron study).[12] The C(4)–C(5) bond length (1.41 (1) Å)

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[10] The lower case letters a, b, and c, etc., prefaced by C, label a specific carbon atom.

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Table II. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations (Esd's) in Parentheses for $[\overline{\text{Pt}\{\text{-C(=O)C(Pr)}}\text{=}\overline{\text{C(Pr)C(Pr)}}\text{=C(Pr)Cl}\}\text{Cl}]_2$ (2a)[a]

	Bond Distances		
Pt–Pt′	3.713 (1)	C(4)–C(13)	1.49 (1)
Pt–Cl(2)	2.540 (2)	C(5)–C(6)	1.52 (1)
Pt–Cl′(2)	2.346 (3)	C(11)–C(12)	1.52 (1)
Pt–C(4)	2.116 (7)	C(12)–C(13)	1.34 (1)
Pt–C(5)	2.099 (8)	C(12)–C(17)	1.50 (1)
Pt–C(17)	1.981 (8)	C(13)–C(14)	1.53 (1)
Cl(1)–C(5)	1.795 (7)	C(17)–O	1.22 (1)
C(3)–C(4)	1.54 (1)	$C-C_{prop}$[b]	1.52 (1)
C(4)–C(5)	1.41 (1)		
	Bond Angles		
Pt–Cl(2)–Pt′	98.86 (9)	Pt–C(5)–Cl(1)	110.7 (4)
Cl(2)–Pt–Cl′(2)	81.14 (8)	Pt–C(17)–O	123.1 (5)
C(4)–Pt–C(17)	81.6 (3)	Cl(1)–C(5)–C(4)	119.3 (4)
C(5)–Pt–C(17)	92.6 (3)	Cl(1)–C(5)–C(6)	108.6 (5)
Cl(2)–Pt–C(17)	171.5 (1)	C(4)–C(5)–C(6)	124.4 (5)
Cl′(2)–Pt–C(17)	90.9 (2)	C(3)–C(4)–C(5)	119.3 (5)
Cl(2)–Pt–C(4)	104.2 (2)	C(3)–C(4)–C(13)	115.1 (5)
Cl′(2)–Pt–C(4)	154.1 (1)	C(5)–C(4)–C(13)	121.6 (5)
Cl(2)–Pt–C(5)	95.8 (2)	C(4)–C(13)–C(12)	118.6 (5)
Cl′(2)–Pt–C(5)	166.9 (1)	C(4)–C(13)–C(14)	117.9 (5)
Pt–C(17)–C(12)	114.1 (5)	C(12)–C(13)–C(14)	123.5 (5)
Pt–C(4)–C(3)	111.4 (4)	C(11)–C(12)–C(13)	126.6 (5)
Pt–C(4)–C(13)	108.5 (5)	C(11)–C(12)–C(17)	118.7 (6)
Pt–C(4)–C(5)	69.9 (4)	C(13)–C(12)–C(17)	114.5 (6)
Pt–C(5)–C(4)	71.1 (4)	C(12)–C(17)–O	122.7 (6)
Pt–C(5)–C(6)	117.1 (4)		
	Torsion Angles[c]		
Pt–C(17)–C(12)–C(13)	−13.8	Cl′(2)–Pt–C(17)–C(12)	−140.3
Pt′–Cl(2)–Pt–C(4)	−154.1	O–C(17)–C(12)–C(13)	168.6
Pt′–Cl(2)–Pt–C(5)	167.2	C(4)–C(13)–C(12)–C(17)	2.0
Cl(2)–Pt–C(4)–C(5)	−81.5	C(4)–Pt–C(17)–C(12)	14.7
Cl(2)–Pt–C(5)–C(4)	105.5	C(5)–Pt–C(17)–C(12)	52.3
Cl′(2)–Pt–C(17)–O	37.3		

[a] Primed atoms are related to unprimed ones by the coordinate transformation: $-x, -y, -z$. [b] Average value; esd's of the mean are estimated according the formula $\sigma(x) = [(\sum_i(x_i - \bar{x})^2/(N - 1)]^{1/2}$ where $\bar{x}$ is the average value and N is the number of observations. [c] Esd's on torsion angles are in the range 1.0–2.0°.

lies in the upper range of the expected distances for coordinated double bonds.[13] We note that this bond length and the values of the angles around atoms C(4) and C(5) (see Table II) may be suggestive of an hybridization approaching sp^3 which is consistent with the large ^1J[Pt–C] coupling constant observed. The atoms bonded to the olefinic atoms are bent away from the metal center, a distortion analogous to that found in the Zeise's salt.[12] It has been suggested that this distortion is due to electronic effects, i.e., d_π–p_π* back-bonding from the Pt atom to the antibonding π* orbital of the olefin. The conformation of the olefinic double bond with respect to the coordination plane, defined by the Pt,Cl(2),Cl′(2) atoms, can be best described by the torsion angles Cl(2)–Pt–C(4)–C(5) of −81.5° and Cl(2)–Pt–C(5)–C(4) of 105.5°, similar to those found in other Pt(II) olefin complexes.[13]

The two bridging chlorine atoms are asymmetrically bonded to the metal center due to the different trans influence of the CO and C=C groups. The shorter Pt–Cl′(2) bond distance (trans to the double bond), 2.346 (3) Å, may be compared with that found in $[Pt(PPh_3)_2Cl\{C(=CH_2)C(Me)=CH_2\}]$,[14] 2.408 (3) Å, with that found in $[(C_7H_{12})PtCl(\mu\text{-}Cl)_2ClPt(C_7H_{12})]$,[15] 2.362 (6) Å, or with the separation found in other square-planar platinum(II) complexes where the trans ligand is a phosphine (in the range 2.37–2.39 Å),[16] suggesting a similar trans influence for the two ligands.

The Pt–Cl(2) distance, 2.540 (2) Å, is one of the longest reported and points to a large trans influence for the acyl group. A similar lenghtening due to the trans influence has been reported in $[Pt(\mu\text{-}Cl)(OMe)(cyclopentadiene)_2]_2$[18] with a Pt–Cl distance of 2.51 Å (trans to an alkyl group). Furthermore, we note that the Pt–C(17) distance (1.981(8) Å) is rather short and indicative of a strong interaction with metal d electrons.[17]

The other bond lengths and angles of the organic moiety are in the expected range, and there are no intermolecular contacts shorter than the sum of the van der Waals radii.

Reactivity of Compound 2a. Compound **2a** cannot be transformed into complex **1a** or degraded to give the free tetrasubstituted cyclopentadienone compound, either by refluxing in toluene or by reacting with ligands such as aliphatic amines, trisubstituted alkyl- or arylphosphines, and alkyl or aryl phosphites. It is interesting to note that this behavior is different from that of the CO-containing products obtained by Maitlis et al.,[4] reacting $Pd(NCC_6H_5)_2Cl_2$ with di-*tert*-butylacetylene, under carbon monoxide atmosphere.

The reaction of complex **2a** (see Scheme II) with 2 equiv of nitrogen- or phosphorus-containing ligands gave, in

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Table III. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for [Pt{CC(Pr)=C(Pr)C(Pr)=C(Pr)O}(PBu$_3$)$_2$Cl][PF$_6$] (11a)

	Bond Distances		
Pt-Cl	2.363 (6)	C(1)-C(2)	1.46 (3)
Pt-P(1)	2.329 (6)	C(2)-C(3)	1.41 (3)
Pt-P(2)	2.324 (6)	C(3)-C(4)	1.34 (3)
Pt-C(1)	1.94 (2)	C(4)-C(5)	1.34 (3)
O-C(1)	1.37 (2)	C-C$^a_{prop}$	1.53 (4)
O-C(5)	1.42 (2)	P-C^a	1.86 (5)
		P-F^a	1.56 (5)
	Bond Angles		
P(1)-Pt-P(2)	172.0 (1)	C(1)-O-C(5)	122.4 (1.1)
C(1)-Pt-Cl	176.3 (2)	C(1)-C(2)-C(3)	117.8 (1.2)
C(1)-Pt-P(1)	94.5 (5)	C(2)-C(3)-C(4)	123.1 (1.2)
C(1)-Pt-P(2)	92.7 (5)	C(3)-C(4)-C(5)	118.9 (1.5)
Cl-Pt-P(1)	86.6 (2)	C-C-C$_{prop}{}^a$	108.8 (2.3)
Cl-Pt-P(2)	85.9 (2)	Pt-P-C^a	112.3 (0.8)
O-C(1)-C(2)	115.9 (1.2)	P-C-C^a	110.8 (1.3)
O-C(5)-C(4)	120.6 (1.4)		

^{a} Average value.

quantitative yields, the monomeric species [Pt{-C(=O)-C(Pr)=C(Pr)C(Pr)=C(Pr)Cl}LCl] (**4a**, L = *p*-toluidine; **5a**, L = piperidine; **6a**, L = triphenylphosphine; **7a**, L = tributylphosphine); no further reaction was observed when compounds **4a** and **5a** reacted with an excess of nitrogen donor ligands. On the other hand, complexes **6a** and **7a** react with phosphorus donor ligands to give a stable pale yellow compound, Pt(CO)(C$_2$Pr$_2$)$_2$Cl$_2$L$_2$ (**8a**, L = PPh$_3$; **9a**, L = PBu$_3$). Compounds **8a** and **9a** can also be obtained by direct reaction of compound **2a** with 4 equiv of triphenylphosphine or tributylphosphine.

When compounds **8** and **9** are treated with a 2-propanol solution of NH$_4$PF$_6$ (see Scheme II), ionic compounds of formula [Pt{CC(R)=C(R)C(R)=C(R)O}L$_2$Cl][PF$_6$] (**10a**, R = Pr, L = PPh$_3$; **11a**, R = Pr, L = PBu$_3$; **11c**, R = Et, L = PBu$_3$) were isolated and fully characterized by elemental analyses and infrared spectra, and the structure of the compound **11a** was clarified by X-ray analysis.

Molecular Structure of [Pt{CC(Pr)=C(Pr)C(Pr)=C(Pr)O}(PBu$_3$)$_2$Cl][PF$_6$] (11a) [Chemical Abstracts index name: (*SP*-4-3)-chloro(3,4,5,6-tetrapropyl-2*H*-pyran-2-ylidene)bis(tributylphosphine)platinum(1+) hexafluorophosphate(1−)]. An ORTEP view of the cation and the atom-labeling scheme are given in Figure 4; bond lengths and angles are reported in Table III. The Pt atom shows a distorted square-planar coordination defined by two trans phosphorus atoms, a chlorine atom, and the C(1) atom of a six-membered carbenic ring, which is rotated with respect to the coordination plane defined by Pt,P(1),P(2),Cl, making a dihedral angle of 77.9°. This value lies in the range 77–90° already reported,[16,19,20] but it is larger than the angle of 63.5° found in the closely related *cis*-[Pt{CC(CO$_2$Et)=C(Ph)C(CO$_2$Et)=C(Ph)O}(PPh$_3$)Cl$_2$].[5] The bond distances involving the Pt atom are best discussed in comparison with the latter compound with a Pt–C(1) bond length of 1.933 (8) Å which is equal to that found in the present work (1.94 (2) Å); other comparable separations have been reported for *cis*-[PtCl$_2${C(NPhCH$_2$)$_2$}PEt$_3$][19a] (Pt–C = 2.01 (1) Å) and *cis*-[PtCl$_2${C(OEt)NHPh}PEt$_3$][19b] (Pt–C = 1.96 (2) Å). These values have been taken to suggest a bond order somewhat greater than 1 compared with an estimated value of 2.02 Å for a Pt(II)–C(sp^2) single bond.[21] The Pt–Cl bond length, 2.363 (6) Å, is also comparable to that found in ref 5 (2.350 (3) Å), while the two Pt–P bond lengths are significantly longer (average value 2.326 (6) Å vs. 2.244 (2) Å)[5] due to the different trans influence of Cl and P atoms.

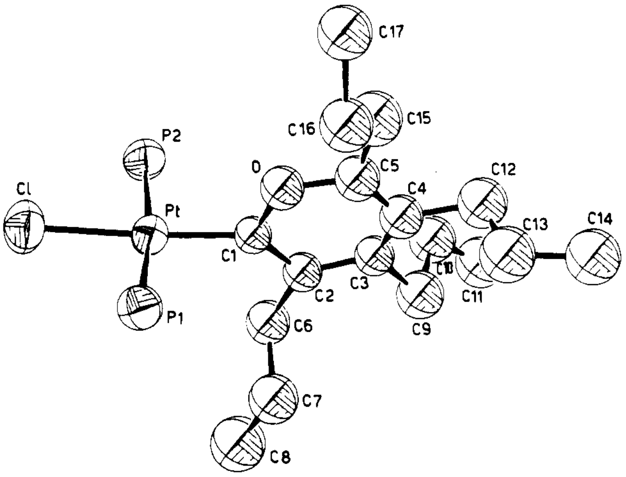

Figure 4. Molecular structure and atom-labeling scheme for [Pt{CC(Pr)=C(Pr)C(Pr)=C(Pr)O}(PBu$_3$)$_2$Cl]$^+$ (**11a**). The butyl groups on the phosphorus atom have been omitted for clarity.

As expected the angles around the Pt atom are different from the ideal value of 90°, the larger angles being C(1)–Pt–P(1) and C(1)–Pt–P(2), due to the steric hindrance of the carbenic ring substituents. The bond distances and angles in the carbenic ring are in the usual range for this type of compounds.[5,22] There are no short intermolecular contacts, and the molecules are held together by van der Waals forces.

NMR Studies. For a study of the possible modifications of the organic fragment bonded to platinum induced by reacting **2** with nitrogen and phosphorus donor ligands, ^{13}C NMR studies on compounds **2a**, **5a**, **7a**, **9a**, and **11c** have been carried out. The NMR spectra of compounds

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(19) (a) Manojlovic-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 2427. (b) Bradley, E. M.; Muir, K. W.; Sim, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1930.

(20) *Molecular Structure and Dimensions*; Cambridge Crystallographic Data Centre, 1972; Vol. A1.

(21) Cardin, C. J.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1977**, 1593.

(22) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(23) Garth, K. R.; Goodfellow, R., J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978; Chapter 8. Mann, B. E.; Taylor, B. F. In *^{13}C NMR Data for Organometallic Compounds*; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic: London, 1981.

2a and **11a**, whose X-ray structures were known, were the starting point to rationalize the other spectra and to suggest the structures of compounds **4–10**.

The derivatives for ^{13}C NMR studies were selected in order to have both high solubility and no overcrowding of the range 80–250 ppm (downfield of $SiMe_4$), useful for structure determination[23] since the resonances of sp^2- and sp-hybridized carbon atoms occur in this region. Obviously the spectra, in the range 0–50 ppm, are, in some cases, complicated by the presence of signals of the four nonequivalent propyl groups superimposed on those of the ligands; therefore the carbon atoms of the propyl groups will not be assigned. Complexes **7a** and **9a** were prepared in situ by reacting **2a** with a stoichiometric amount of the ligand; the spectra were closely related to those obtained from PPh_3 derivatives **6a** and **8a**.

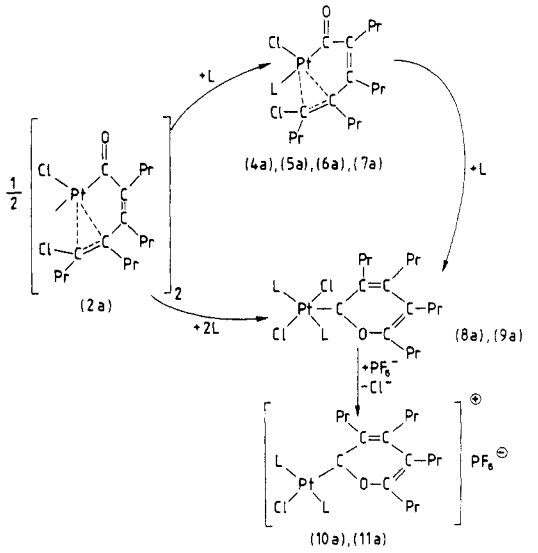
In Table I we report some of the relevant chemical shifts and coupling constants for compounds **2a**, **5a**, **7a**, **9a**, and **11c** together with the numbering scheme of significant carbon atoms; the spectra of these derivatives are schematically shown in Figure 1.

The ^{13}C NMR spectrum of compound **2a** (Table I) is fully consistent with the solid-state structure and shows the expected five signals (in the range 80–250 ppm). Four of the signals are coupled with ^{195}Pt, but not the one with a chemical shift of δ 162.4; this value is consistent with a carbon atom in the β-position, with respect to a conjugate carbonyl group, and therefore is assigned to atom C(c).[10] The other four signals have been assigned on the basis of the chemical shifts and coupling constants. Assuming that a coupling constant around 1000 Hz is typical for a carbon atom σ bonded to platinum[1,5] we assigned the signal at δ 184.6 to atom C(a). Assuming that a coupling constant around 300 Hz is in agreement with carbon atoms π bonded to platinum, we assigned the signals at δ 93.7 and 106.1 to atoms C(d) and C(e), respectively. The last signal at δ 148.6 is therefore due to C(b). In this case, 12 resonances, belonging to the propyl fragments, were clearly detected in the region 0–50 ppm (Table I).

The ^{13}C NMR spectra of compounds **5a** and **7a** showed the same pattern found in complex **2a**, with small variations in the chemical shifts and coupling constants for C(a), C(b), and C(c) carbon atoms. The ^{13}C NMR spectrum of compound **7a** showed also additional coupling with ^{31}P; the ^2J(P–C) values suggest, for the phosphine ligand,[24] a trans arrangement with respect to the coordinated double bond. In compounds **2a**, **5a**, and **7a** in Pt–C coupling constants of the carbon atoms bonded to platinum decrease significantly in order, particularly for the atoms C(d) and C(e); this may be explained by an increasing of the trans influence of the ligand possibly associated with some polarization of the organic fragment which can also account for the very low CO stretching frequencies found in compounds **5a**, **6a**, and **7a**.

The ^{13}C NMR spectra of compounds **7a** and **9a** are significantly different, both in chemical shifts and in coupling constants, and **9a** cannot be rationalized on the basis of a simple addition to platinum of a second ligand, associated with the breaking of the π bond. On the other hand, the ^{13}C NMR spectra of compounds **11c** and **9a** (see Table I and Figure 1) are essentially identical, in the 80–250 ppm region, thus suggesting the presence in **9a** of the same cyclic carbene ligand found in the ionic complex **11a**. The carbene ligand is formed by ring closure between the oxygen, of the acylic carbonyl group, and carbon C(e), with concerted elimination of the chlorine atom from carbon C(e) followed by its addition to platinum. In compound **9a** the signal of the C(a) carbon σ bonded to platinum [$^1J(^{195}$Pt–C) = 1349 Hz] clearly shows additionally the triplet due to the coupling with two tributylphosphines in a trans position [$^2J(^{31}$P–C) = 9 Hz]. Further support of this arrangement of the phosphine ligands around platinum comes from the ^{31}P NMR spectrum, which shows a unique signal at δ 8.92, downfield of the standard, with a $^1J(^{195}$Pt–^{31}P) = 2407 Hz.

Scheme II. Reactivity of Compound 2a[a]



[a] **4a**, L = *p*-toluidine; **5a**, L = piperidine; **6a**, L = triphenylphosphine; **7a**, L = tributylphosphine; **8a**, L = triphenylphosphine; **9a**, L = tributylphosphine; **10a**, L = triphenylphosphine; **11a**, L = tributylphosphine.

Compound **9a** was prepared in situ (see Experimental Section) and cannot be isolated as solid material, whereas the closely related **8a**, having a different phosphine ligand, can be obtained only as a powder. The FAB mass spectrum shows the [M − ^{35}Cl]$^+$ ion and confirms, for the solid state, the molecular formula of complex **8a** with two triphenylphosphine ligands bonded to platinum. The ^{13}C NMR spectrum of **8a** shows the same signals as compound **9a** both in chemical shifts and in coupling constants (in the region free from PPh_3 signals). In particular, carbon C(a) {δ 200.6 [$^2J(^{31}$P–C) = 9 Hz, $^1J(^{195}$Pt–C) not detected]} bonded to platinum appears as a triplet due to the coupling with two equivalent phosphorus atoms. Conductivity measurements in different polar solvents on **8a** rule out an 1:1 electrolyte, and therefore the two chlorine atoms are both coordinated to platinum. These data suggest that both in **8a** and in **9a** a pentacoordinate derivative is present: $[\mathrm{Pt}\{\overline{\mathrm{CC(Pr){=}C(Pr)C(Pr){=}C(Pr)O}}\}\mathrm{L_2Cl_2}]$ (**8a**, L = PPh_3; **9a**, L = PBu_3) (see Scheme II). However, the apparent molecular mass (vapor pressure) of **8a**, in dilute solution, of different solvents gives values corresponding to half of the calculated value, indicating a complete dissociation of compound **8a** in solution. This result is in agreement with the ^{31}P NMR spectrum, in $CDCl_3$, at room temperature, which unlike that of **9a** shows free PPh_3 together with a signal, coupled with platinum {δ 30 [$^1J(^{195}$Pt–P) = 4340 Hz]}, that could be attributed to a tetracoordinate monophosphine derivative and a very broad signal at δ 22 attributed to the pentacoordinated compound **8a**. By addition of PPh_3 to the solution of **8a**, the resonance of the uncoordinated ligand is enhanced, while the signal coupled with Pt disappears and no other signals can be detected, due probably to an exchange process. The

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[24] Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247. Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979.

low-temperature (190 K; acetone-d_6) ^{31}P NMR spectrum of **8a** shows a nonbinomial triplet at δ 22 [$^1J(^{195}\text{Pt–P}) = 3600$ Hz], expected for two equivalent phosphorus atoms coupled with platinum. Moreover, the ^{195}Pt NMR spectrum of **8a**, at room temperature, showed the presence of a doublet at δ −2640 [$^1J(^{31}\text{P–Pt}) = 4340$ Hz] and a triplet at δ −3266 [$^1J(^{31}\text{P–Pt}) = 3600$ Hz] due to different platinum complexes attributed to the tetracoordinate monophosphine derivative and to the pentacoordinate bis(phosphine) compound **8a**, respectively, in keeping with the corresponding values of the coupling constants found in the ^{31}P NMR. We may therefore conclude that the pentacoordinate compound **8a** is stable only in the solid state, whereas compound **9a** is stable as a pentacoordinate derivative also in solution. The different behavior between **8a** and **9a**, in solution, can be explained by the different basicity and the steric hindrance of PBu_3 and PPh_3.[25] On the other hand both compounds **8a** and **9a** are transformed, in the presence of NH_4PF_6, into the ionic complexes **10a** and **11a** where an identical stable tetracoordinate bis(phosphine) cation is present.

CO Insertion Products in the 2-Butyne and 3-Hexyne Reactions. The results obtained with 4-octyne suggest that the CO-containing products, obtained from $Pt(CO)_2Cl_2$ and 2-butyne or 3-hexyne, could be in general analogous to those obtained from 4-octyne. By reacting 2-butyne with $Pt(CO)_2Cl_2$, it was possible to isolate compound **2b** in very low yield, together with $[Pt_2(C_2Me_2)_4Cl_3][Pt(CO)Cl_3]$.[6] The ^{13}C NMR spectrum of compound **2b** showed the same spectrum of **2a** in the region of 80–250 ppm [C(b), 142.3, C(c), 158.9, C(d), 87.4, C(e), 99.8 ppm],[26] suggesting the presence of an analogous organic fragment. When these findings are taken into account, compound **2b**, previously formulated as a nonsymmetrically bonded tetramethylcyclopentadienone,[6] should be reformulated. The ^{1}H NMR spectrum of **2b**[6] shows four signals due to the resonances of the four nonequivalent methyl groups, fully consistent with the type of structure found for the 4-octyne derivative **2a**.

A Diels–Alder type compound, obtained by dimerization of a tetramethylcyclopentadienone derivative, from reaction of $Pt(CO)_2Cl_2$ and 2-butyne, was isolated and fully characterized by elemental analysis, mass spectrum, and IR and ^{1}H and ^{13}C NMR spectra. In this case we did not observe the formation of a Pt(II) η^4-tetramethylcyclopentadienone complex which is probably the intermediate species responsible for the formation of the free tetramethylcyclopentadienone.

The same reaction pattern observed for 4-octyne was also found in the case of 3-hexyne; thus it is possible to isolate, together with $[Pt_2(C_2Et_2)_4Cl_3][Pt(CO)Cl_3]$,[6] the yellow **1c** and the white **2c** compounds. Again compounds **1c**, **2c**, and the derivatives obtained from these two complexes should be reformulated on the basis of analytical and spectroscopic data and by comparison with the result obtained for 4-octyne. The reaction to give the ionic cyclocarbene derivative $[(Pt\{\overline{CC(Et){=}C(Et)C(Et){=}C(Et)O}\}(PBu_3)_2Cl][PF_6]$ (**11c**) has been carried out by reacting compound **2c** with stoichiometric amounts of tributylphosphine and NH_4PF_6. The ^{13}C NMR spectrum of compound **11c** (Table I) showed the expected five signals (in the region 80–250 ppm) fully consistent with the structure found in the case of compound **11a**.

Conclusive Remarks

Several attempts have been done to optimize the yields of compounds **1** and **2** by carrying out the reaction under carbon monoxide atmosphere, changing the molar ratio of $Pt(CO)_2Cl_2$ to alkyne and/or solvent (e.g., heptane, where the two compounds are insoluble), but in all cases there was not a significant variation in the quantity of isolated products. $[Pt_2(C_2Pr_2)_2Cl_3][Pt(CO)Cl_3]$ is the only product when the reaction is carried out in $CHCl_3$ and the major one when the reaction is carried out in toluene and heptane.

Scheme I reports the possible pathways of the reaction of $Pt(CO)_2Cl_2$ with R–C≡C–R (R = Me, Et, Pr) showing the formation of the isolated compounds. The formation of $[Pt_2(C_2R_2)_4Cl_3][Pt(CO)Cl_3]$ is in agreement with the mechanism proposed by Maitlis for the formation of cyclobutadiene palladium(II) derivatives.[4] Compound **2**, formed by the insertion of a terminal CO group originally bonded to platinum, was previously proposed as the intermediate species in the formation of cyclopentadienone palladium compounds.[4] In our case compound **2** is stable and cannot be transformed into a cyclopentadienone compound, whereas this transformation has been postulated for the palladium derivative. We suggest, therefore, that the reaction giving the platinum cyclopentadienone compound **1** follows a different route (see Scheme I). We propose the insertion of a molecule of acetylene, followed by CO insertion, to give species **d** which inserts a second molecule of acetylene to give **e**. This intermediate derivative is responsible for the formation of platinum(II) cyclopentadienone complexes (**1a**, R = C_3H_7; **1c**, R = C_2H_5) via the cyclization of the organic fragment; in the case of 2-butyne, product **1b** should be the instable intermediate responsible for the formation of the free cyclopentadienone.

Experimental Section

General Comments. Microanalyses and molecular weights were determined by Laboratorio Analisi Universitá di Milano and by Pascher Mikroanalytisches Laboratorium Bonn.

^{1}H and ^{13}C {^{1}H} nuclear magnetic resonance (NMR) spectra (Table I) were recorded on a Bruker WP 80 spectrometer, operating at 80 MHz for proton and at 20.14 MHz for carbon, or on a Varian XL-200 spectrometer, operating at 200 MHz for proton and at 50.3 MHz for carbon, and are reported as parts the million (ppm) downfield from the internal standard Me_4Si. In Figure 1 a schematic view of ^{13}C NMR spectra of selected compounds is reported; for clarity the signals, obtained with different spectrometers, are scaled to a spectrometer operating at 20.14 MHz for carbon. ^{31}P NMR spectra has been recorded on a Bruker WP 80 spectrometer operating at 32.4 MHz and are reported downfield to the external standard (H_3PO_4, 85% in D_2O).

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer, calibrated with polystyrene film, or on a Nicolet MX-1 FT-IR Fourier transform interferometer using Nujol mulls and NaCl or CsI plates. Abbreviations: v, very; s, strong; w, weak; m, medium; sh, shoulder. Electron-impact mass spectra were registered by using a Varian MAT 112 mass spectrometer, calibrated against known masses of perfluorokerosene, with a source voltage of 70 eV and probe temperature in the 100–200 °C range. FAB mass spectra were registered by using a V.G. 7070 EQ mass spectrometer equipped with H.F. magnet and standard FAB source with xenon gas at 8 keV (sulfolane and glycerine mull).

Conductivity was determined on a Philips PR 9500 bridge. All the reactions were conducted under a nitrogen atmosphere by using the Schlenk tube technique and with anhydrous solvents although the products were rarely air-sensitive. Solvents were purified and dried by standard methods. Reactions of $Pt(CO)_2Cl_2$ with 4-octyne, 3-hexyne, and 2-butyne in toluene were performed as previously reported.[6,7] *cis*-$Pt(CO)_2Cl_2$ was prepared as previously described.[27]

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[25] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[26] Owing to difficulties to obtain a large amount of pure compound the ^{13}C NMR spectrum does not allow us to detect the C(a) resonance and the ^{195}Pt–C coupling constants.

Reaction of $Pt(CO)_2Cl_2$ with 4-Octyne in Heptane and Synthesis of $[Pt\{\eta^4\text{-}C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)\}Cl_2]$ (1a) and $[Pt\{-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl\}Cl]_2$ (2a). To a suspension of $Pt(CO)_2Cl_2$ (3.66 g, 11.37 mmol) in heptane (140 mL), under a positive pressure of nitrogen, was added 4-octyne (7.1 mL, 48.32 mmol), and the suspension was stirred at room temperature. The disappearance of $Pt(CO)_2Cl_2$ was conveniently monitored by IR spectroscopy, and when all the carbonyl had reacted (over a period of 3 days), the solid material was filtered off and treated with cold acetone (10 mL; -20 °C). The white solid residue was filtered off and crystallized from acetone to give **2a**: 0.780 g (yield 13.4%); MS, *m/e* 478 [$M^+/2 - Cl$; ^{195}Pt, ^{35}Cl]; molecular weight calculated 1028.80; vapor pressure molecular weight 966 (5.1178 mg, 0.7666 g of $CHCl_3$); IR (cm^{-1}, Nujol mull) 1689 (s), 1635 (w), 290 (w), 275 (sh). Anal. Calcd for $C_{34}H_{56}Cl_4O_2Pt_2$: C, 39.69; H, 5.49; Cl, 13.78; O, 3.11; Pt, 37.92. Found: C, 39.65; H, 5.51; Cl, 13.75; O, 3.33; Pt, 37.6.

The acetone was removed under reduced pressure, and the residue was treated with hexane (20 mL). The solid was then filtered off and washed with hexane (3 × 10 mL). The known $[Pt_2(C_2Pr_2)_4Cl_3][Pt(CO)Cl_3]$ complex (1.37 g, 28.5%) was obtained. The heptane mother solution was evaporated to dryness under vacuum. The residual pale yellow oil was pumped at 40 °C for 4 h, and the viscous semisolid material was treated with hexane (30 mL) and vigorously stirred for 3 h. The brown solid was filtered off and washed with hexane (3 × 10 mL), and the solid was extracted with acetone (2 × 10 mL) to give after cooling some more of the compound **2a**. An excess of 2-propanol was added to the acetone extracts, and a yellow microcrystalline solid was obtained. Compound **1a**: 0.640 g (yield 10.9%); MS, *m/e* 513 [M^+; ^{195}Pt, ^{35}Cl]; 514.40; IR (cm^{-1}, Nujol mull) 1710 (s) [$\nu(C=O)$], 343 (w), 333 (sh), [$\nu(Pt-Cl)$]. Anal. Calcd for $C_{17}H_{28}Cl_2OPt$: C, 39.69; H, 5.49; Cl, 13.78; O, 3.11; Pt, 37.92. Found: C, 39.51; H, 5.49; Cl, 13.75; O, 3.29; Pt, 38.3.

Preparation of $[Pt\{\eta^4\text{-}C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)\}(p\text{-}NH_2C_6H_4CH_3)Cl_2]$ (3a). To a solution of **1a** (0.146 g, 0.284 mmol) in toluene (10 mL) was added *p*-toluidine (0.052 g, 0.58 mmol) dissolved in toluene (10 mL), and the solution was stirred at room temperature for 2 h. After concentration to small volume (~2 mL) and hexane addition, a yellow product was filtered off, washed with hexane (3 × 10 mL) and recrystallized from CH_2Cl_2 and heptane to give **3a**: 0.169 g (yield 96%); IR (cm^{-1}, Nujol mull) 1690 (vs) [$\nu(C=O)$], 1575 (m), 1510 (s). Anal. Calcd for $C_{24}H_{37}Cl_2PtNO$: C, 46.45; H, 5.87; N, 2.25. Found: C, 45.79; H, 5.85; N, 2.53.

Reaction of 1a with PPh_3. To a suspension of **1a** (0.091 g, 0.177 mmol) in hexane (10 mL) was added PPh_3 (0.098 g, 0.369 mmol) dissolved in hexane (15 mL). Instantaneously a white precipitate was formed. After the solution was stirred for 2 h, the white precipitate was filtered off, washed with hexane (3 × 10 mL), and dried. The compound was identified as $Pt(PPh_3)_2Cl_2$ by comparison with an authentical sample (yield 70%).

The orange hexane solution was dried on a rotary evaporator, and the yellow solid was identified from the mass spectrum (M^+ 248) as tetrapropylcyclopentadienone derivative: IR (cm^{-1}, Nujol mull) 1710 (s) [$\nu(C=O)$]. The yellow solid is unstable at room temperature and slowly transformed into its white Diels–Alder derivative: IR (cm^{-1}, Nujol mull) 1770 (s), 1735 (m), 1695 (w).

Preparation of $[Pt\{-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl\}(NH_2C_6H_4CH_3)Cl]$ (4a). To a solution of **2a** (0.117 g, 0.144 mmol) in CH_2Cl_2 (8 mL) was added *p*-toluidine (0.032 g, 0.30 mmol), and the solution was stirred at room temperature for 1 h to drive the reaction to completion. After hexane addition (5 mL) and concentration under vacuum, a white precipitate was obtained, filtered off, washed with hexane (3 × 10 mL), and dried. The white compound was recrystallized from CH_2Cl_2 and hexane to give complex **4a**: 0.076 g (yield 53%); IR (cm^{-1}, Nujol mull) 1620 (s), 1565 (s), 1520 (s), 265 (m). Anal. Calcd for $C_{24}H_{37}Cl_2NOPt$: C, 46.38; H, 6.00; N, 2.25. Found: C, 46.54; H, 5.98; N, 2.30.

Preparation of $[Pt\{-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl\}(C_5H_{11}N)Cl]$ (5a). To a suspension of compound **2a** (0.256 g, 0.25 mmol) in hexane (20 mL) was added piperidine (0.060 mL, 0.607 mmol); instantaneously the solution became clear and was stirred at room temperature for 2 h. After being concentrated to a smaller volume (5 mL) and cooled to -20 °C, a pale yellow precipitate was obtained, filtered, washed with hexane (3 × 5 mL), and dried. Compound **5a**: 0.258 g (yield 85 %); IR (cm^{-1}, Nujol mull) 1640 (m), 1630 (m), 1605 (s), 365 (vw), 270 (m) [$\nu(Pt-Cl)$]. Anal. Calcd for $C_{22}H_{39}Cl_2NOPt$: C, 44.07; H, 6.56; N, 2.34. Found: C, 43.70; H, 6.40; N, 2.61.

Preparation of $[Pt\{-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl\}(PPh_3)Cl]$ (6a). To a solution of compound **2a** (0.391 g, 0.38 mmol) in toluene (10 mL) was added PPh_3 (0.2 g, 0.77 mmol; 5 mL of toluene), and the solution was stirred at room temperature for 2 h. After the solution was concentrated under vacuum to a small volume (2 mL) and hexane added, a white solid precipitated. This was filtered, washed with hexane (2 × 10 mL), and dried. The compound was recrystallized from CH_2Cl_2 and heptane to give **6a**: 0.308 g (yield 52%); IR (cm^{-1}, Nujol mull) 1656 (s), 1635 (m), 340 (vw), 265 (m); molecular weight calculated 776.69, found 716 (vapor pressure; CH_2Cl_2 solution, concentration in the range 3–7 g/L). Anal. Calcd for $C_{35}H_{43}Cl_2OPPt$: C, 54.12; H, 5.58; Cl, 9.13; O, 2.06; P, 3.99; Pt, 25.12. Found: C, 54.27; H, 5.63; Cl, 8.97; O, 2.42; P, 3.92; Pt, 24.5.

Preparation of $[Pt\{-C(=O)C(Pr)=C(Pr)C(Pr)=C(Pr)Cl\}(PBu_3)Cl]$ (7a). A $CDCl_3$ solution of compound **7a** has been obtained by treating, under nitrogen atmosphere, pure compound **2a** (0.245 g, 0.238 mmol) with a stoichiometric amount of PBu_3 (0.12 mL, 0.488 mmol).

Preparation of $[Pt\{CC(Pr)=C(Pr)C(Pr)=C(Pr)O\}(PPh_3)_2Cl_2]$ (8a). PPh_3 (0.178 g, 0.677 mmol) dissolved in hexane (40 mL) was added dropwise under stirring to a suspension of **2a** (0.165 g, 0.160 mmol) in hexane (10 mL). The suspension became first yellow and clear, but after 5 min the solution became cloudy while a pale yellow material was formed. The suspension was stirred for 3 h, to drive the reaction to completion. The resulting yellow precipitate was filtered off, washed with hexane (3 × 10 mL), and dried. Compound **8a**: 0.270 g (yield 82%); $\Lambda_m = 12\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 0.98×10^{-3} M acetone solution, $\Lambda_m = 0.87\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 0.91×10^{-3} M nitrobenzene solution, $\Lambda_m = 0.38\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 0.7×10^{-3} M chloroform solution; FAB mass spectrum, positive mode, molecular ion 1004 equal to molecular weight - ^{35}Cl (molecular weight calculated for ^{195}Pt and ^{35}Cl); molecular weight calculated 1039, found 516 (vapor pressure determination in $CHCl_3$ solution, 11.689 mg of **8a**, and 0.9375 of $CHCl_3$), found 554 (vapor pressure determination in toluene solution, 3.147 mg of **8a**, and 0.3449 g of toluene); IR (cm^{-1}, Nujol mull) 1625 (s), 1565 (w), 260 (mw) [$\nu(Pt-Cl)$]. Anal. Calcd for $C_{53}H_{58}Cl_2OP_2Pt$: C, 61.27; H, 5.63; Cl, 6.82; O, 1.54; P, 5.96; Pt, 18.77. Found: C, 60.32; H, 5.51; Cl, 7.55; O, 2.88; P, 5.94; Pt, 18.4.

Preparation of $[Pt\{CC(Pr)=C(Pr)C(Pr)=C(Pr)O\}(PBu_3)_2Cl_2]$ (9a). A $CDCl_3$ solution of compound **9a** was obtained by treating under nitrogen atmosphere a pure compound **2a** (0.245 g, 0.238 mmol) with the stoichiometric amount of PBu_3 (0.25 mL, 1.01 mmol).

Preparation of $[Pt\{CC(Pr)=C(Pr)C(Pr)=C(Pr)O\}(PPh_3)_2Cl\}][PF_6]$ (10a). A solution of 2-propanol (30 mL) containing NH_4PF_6 (0.250 g, 1.5 mmol) was treated with a solution of **8a** (0.5 g, 0.48 mmol). Immediately a white solid was obtained, and the suspension was stirred for an additional 20 min. The white precipitate was filtered off, washed with cold 2-propanol (2 × 10 mL, -20 °C), and dried. **10a**: 0.360 g (yield 80%); IR (cm^{-1}, Nujol mull) 1580 (m), 835 (s), 307 (m) [$\nu(Pt-Cl)$]; $\Lambda_m = 131\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 0.67×10^{-3} M acetone solution. Anal. Calcd for $C_{53}H_{58}ClF_6OP_3Pt$: C, 55.43; H, 5.09; Cl, 3.09; O, 1.39; F, 9.92; P, 8.09; Pt, 16.99. Found: C, 54.05; H, 5.15; Cl, 3.14; F, 9.7; O, 2.5; P, 8.13; Pt, 16.6.

Preparation of $[Pt\{CC(Pr)=C(Pr)C(Pr)=C(Pr)O\}(PBu_3)_2Cl][PF_6]$ (11a). Compound **11a** was prepared in a similar way to **10a**, treating **9a** (0.438 g, 0.437 mmol) with a saturated 2-propanol solution (10 mL) of NH_4PF_6. **11a**: 0.245 g (yield 50%); $\Lambda_m = 120\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 1.024×10^{-3} M acetone solution.

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(27) Schutzenberger, P. *Ann. Chim. Phys.* **1870**, *21*, 356. *J. Prakt. Chem.* **1871**, *21*, 165. Irving, R. J.; Magnusson, E. A. *J. Chem. Soc., Dalton Trans.*, **1956**, 1860.

Table IV. Crystal Data and Intensity Collection Parameters for 2a and 11a

	2a	11a
formula	$C_{34}H_{56}Cl_4O_2Pt_2$	$C_{41}H_{82}ClF_6OP_3Pt$
fw	1028.81	1028.57
cryst system:	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	8.256 (2)	25.394 (6)
b, Å	10.293 (3)	14.897 (4)
c, Å	12.632 (3)	13.858 (3)
α, deg	73.50 (2)	90.0
β, deg	76.50 (1)	90.0
γ, deg	81.62 (2)	90.0
V, Å^3	997.2	5242.4
Z	1	4
F_{000}	500	2088
d(calcd), g cm^{-3}	1.713	1.303
d(obsd), g cm^{-3}	1.72	1.28
radiatn Mo K$\bar{\alpha}$	graphite monochromated, λ = 0.71069 Å	
abs coeff, cm^{-1}	73.8	28.9
θ range	$3.0 \leq \theta \leq 25.0$	$2.5 \leq \theta \leq 22.0$
scan type	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg s^{-1}	0.04	0.04
scan width, deg	1.2	1.1
total bkgd time, s	14	16
receiving aperture (hor, deg)	1.0	1.0
receiving aperture (vert, deg)	1.0	1.0
no. of data collected	3507	3603
no. of obsd data ($I_{net} > 3\sigma(I)$)	2762 ($\pm h,\pm k,+l$)	2198 ($+h,+k,+l$)
no. of parameters refined	190	238
R^a	0.034	0.057
$R_w{}^b$	0.055	0.064
goodness of fit^c	0.63	0.72

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m = number of data used and n = number of parameters varied.

Anal. Calcd for $C_{41}H_{82}ClF_6OP_3Pt$: C, 47.7; H, 8.04. Found: C, 46.15; H, 8.04.

Preparation of [Pt{CC(Et)═C(Et)C(Et)═C(Et)O}(PBu$_3$)$_2$Cl][PF$_6$] (11c). To a suspension of **2c** (0.306 g, 0.655 mmol) in 2-propanol (20 mL) was added PBu_3 (0.34 mL, 1.38 mmol) dropwise, and the solution was stirred at room temperature. The complex was metathesized with a solution of NH_4PF_6 (0.18 g, 1.1 mmol; 20 mL of 2-propanol). After concentration to a small volume (10 mL) a white solid was formed, filtered off, washed with cold 2-propanol (2 × 5 mL), and dried. **11c**: 0.4 g (yield 63%); IR (cm^{-1}, Nujol mull) 1580 (m), 835 (s), 307 (m). Anal. Calcd for $C_{37}H_{74}ClF_6OP_3Pt$: C, 45.7; H, 7.67. Found: C, 45.64; H, 7.58.

Formation of Diels–Alder Type Derivative from the Reaction of Pt(CO)$_2$Cl$_2$ and 2-Butyne. To a suspension of $Pt(CO)_2Cl_2$ (1.66 g, 4.13 mmol) in heptane (50 mL) was added 2-butyne (4 mL, 51 mmol), and the suspension was stirred at room temperature for 3 days to drive the reaction to completion. The yellow solid material was filtered off, washed with heptane (3 × 10 mL), and dried to give $[Pt_2(C_2Me_2)_4Cl_3][Pt(CO)Cl_3]$. The heptane was removed under reduced pressure, and the residue was pumped at 40 °C for 3 h. The oily residue was dissolved with hexane (30 mL), and after cooling (–20 °C) the solution gave an ivory solid. The compound was filtered off, washed with cold hexane (2 × 20 mL, –20 °C), and recrystallized from acetone and 2-propanol to give the Diels–Alder organic compound (1.4 g, yield 50% an alkyne): IR (Nujol mull, cm^{-1}) 1760 (s), 1690 (s), 1540 (m); MS, *m/e* 272, 216 [M – 56], 201 [M – 71], 186 [M – 86], 171 [M – 101], 156 [M – 116]; mp 192 °C; ^{1}H NMR ($CDCl_3$) 1.95 (q, 3 H), 1.63 (q, 6 H), 1.59 (s, 3 H), 1.26 (s, 3 H), 1.2 (s, 3 H), 1.04 (s, 3 H), 0.9 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 207.96 (C═O), 205.46 (C═O), 168.92 (1 C), 139.99 (1 C), 134.90 (1 C), 133.97 (1 C), 58.96 (1 C), 57.78 (1 C), 53.79 (1 C), 52.68 (1 C), 14.23 (1 CH_3), 14.18 (1 CH_3), 13.86 (1 CH_3), 10.59 (2 CH_3), 8.45 (1 CH_3), 8.23 (1 CH_3), 7.47 (1 CH_3). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.3; H, 8.6.

Crystallography

Crystals suitable for X-ray diffraction of compounds **2a** and **11a** were obtained by slow diffusion of hexane into dichloromethane solutions. Data were collected on a Philips PW 1100 diffractometer. Table IV lists data collection and unit cell parameters for compounds **2a** and **11a**. Data were corrected for Lorentz and polarization factors and for absorption; intensities were considered as observed if $I_{net} > 3\ \sigma\ (I_{tot})$. The structures were solved by a combination of Patterson and Fourier methods and refined by block diagonal least squares using a Cruickshank weighting scheme and demanding that no systematic trend is present in the weights when analyzed in batches of increasing $|F_o|$ and $(\sin\theta)/\lambda$. The function minimized was $[\sum w(|F_o| - 1/k|F_c|)^2]$.[28] No extinction correction was found necessary on both sets of data.

Table V. Positional Parameters and Their Estimated Standard Deviations for [Pt{-C(═O)C(Pr)═C(Pr)C(Pr)═C(Pr)Cl}Cl]$_2$ (2a)

atom	x	y	z
Pt	0.01014 (4)	–0.13838 (3)	0.13043 (3)
Cl(1)	–0.0125 (3)	–0.2084 (2)	0.3975 (2)
Cl(2)	0.1598 (3)	0.0666 (2)	0.0041 (2)
C(1)	0.5554 (16)	–0.3015 (13)	–0.0480 (10)
C(2)	0.3808 (12)	–0.3070 (9)	0.0253 (7)
C(3)	0.3704 (9)	–0.2551 (8)	0.1287 (6)
C(4)	0.1972 (9)	–0.2672 (7)	0.2080 (6)
C(5)	0.1316 (9)	–0.1656 (7)	0.2647 (6)
C(6)	0.2272 (11)	–0.0496 (8)	0.2632 (7)
C(7)	0.3516 (13)	–0.0967 (9)	0.3444 (8)
C(8)	0.4579 (22)	0.0119 (14)	0.3388 (14)
C(9)	–0.1695 (21)	–0.7599 (16)	0.2477 (15)
C(10)	–0.0827 (17)	–0.6297 (13)	0.2053 (10)
C(11)	–0.0976 (11)	–0.5588 (9)	0.2969 (7)
C(12)	–0.0157 (10)	–0.4260 (8)	0.2516 (6)
C(13)	0.1420 (9)	–0.4074 (7)	0.2517 (6)
C(14)	0.2667 (10)	–0.5222 (7)	0.2996 (7)
C(15)	0.2820 (10)	–0.5164 (8)	0.4165 (7)
C(16)	0.4023 (12)	–0.6335 (9)	0.4668 (8)
C(17)	–0.1202 (10)	–0.2977 (8)	0.2093 (7)
O	–0.2713 (7)	–0.2935 (7)	0.2194 (6)

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[28] Cruickshank, D. W. J. In *Computing Methods in Crystallography*; Ahmed, A., Ed.; Munksgaard: Copenhagen. For references to least squares, Fourier, and structure factor calculation programs see: Albinati A.; Bruckner S. *Acta Crystallogr., Sect B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3390.

Table VI. Positional Parameters and Their Estimated Standard Deviations for $[\mathrm{Pt}\{\overline{\mathrm{CC(Pr)}{=}\mathrm{C(Pr)C(Pr)}{=}\mathrm{C(Pr)O}}\}(\mathrm{PBu_3})_2\mathrm{Cl}][\mathrm{PF_6}]$ (11a)

atom	*x*	*y*	*z*
Pt	0.16435 (3)	0.10240 (6)	0.05668 (5)
P(1)	0.2479 (2)	0.1126 (5)	−0.0119 (4)
P(2)	0.0870 (2)	0.0908 (5)	0.1455 (4)
P(3)	0.4603 (3)	0.0742 (7)	−0.0031 (6)
Cl	0.2063 (2)	0.0379 (5)	0.1922 (4)
C(1)	0.1291 (6)	0.1622 (11)	−0.0498 (14)
C(2)	0.0963 (7)	0.1275 (12)	−0.1274 (13)
C(3)	0.0720 (7)	0.1902 (13)	−0.1896 (13)
C(4)	0.0842 (8)	0.2776 (14)	−0.1903 (15)
C(5)	0.1119 (8)	0.3114 (15)	−0.1169 (15)
C(6)	0.0907 (8)	0.0244 (15)	−0.1279 (16)
C(7)	0.1275 (9)	−0.0169 (17)	−0.2043 (18)
C(8)	0.1188 (10)	−0.1208 (20)	−0.1995 (20)
C(9)	0.0345 (9)	0.1452 (16)	−0.2663 (18)
C(10)	−0.0247 (9)	0.1552 (17)	−0.2237 (17)
C(11)	−0.0626 (9)	0.1331 (17)	−0.2922 (18)
C(12)	0.0607 (9)	0.3460 (17)	−0.2640 (18)
C(13)	0.0982 (10)	0.3532 (18)	−0.3388 (21)
C(14)	0.0723 (15)	0.4042 (30)	−0.4296 (30)
C(15)	0.1231 (9)	0.4097 (19)	−0.0920 (17)
C(16)	0.1674 (15)	0.4257 (25)	−0.0765 (29)
C(17)	0.1679 (16)	0.5283 (27)	−0.0046 (28)
C1P1	0.2911 (7)	0.1829 (14)	0.0595 (17)
C12P1	0.2674 (9)	0.2744 (17)	0.0695 (19)
C13P1	0.3013 (12)	0.3353 (23)	0.1446 (24)
C14P1	0.2857 (15)	0.4198 (27)	0.1531 (29)
C2P1	0.2840 (10)	0.0038 (18)	−0.0074 (19)
C22P1	0.2521 (9)	−0.0704 (16)	−0.0514 (19)
C23P1	0.2834 (12)	−0.1675 (22)	−0.0434 (24)
C24P1	0.2524 (16)	−0.2442 (27)	−0.0885 (30)
C3P1	0.2439 (10)	0.1609 (18)	−0.1443 (20)
C32P1	0.2933 (14)	0.1791 (26)	−0.1823 (27)
C33P1	0.2810 (13)	0.2201 (24)	−0.2884 (26)
C34P1	0.2609 (14)	0.3096 (27)	−0.2963 (27)
C1P2	0.0906 (10)	0.1641 (17)	0.2508 (18)
C12P2	0.0998 (14)	0.2654 (25)	0.2169 (28)
C13P2	0.1084 (16)	0.3153 (30)	0.3009 (31)
C14P2	0.1210 (15)	0.4146 (29)	0.2673 (28)
C2P2	0.0252 (8)	0.1241 (14)	0.0803 (15)
C22P2	−0.0257 (11)	0.1155 (22)	0.1476 (22)
C23P2	−0.0752 (10)	0.1371 (18)	0.0594 (22)
C24P2	−0.1228 (14)	0.1286 (26)	0.1279 (27)
C3P2	0.0756 (9)	−0.0195 (17)	0.1959 (18)
C32P2	0.0712 (10)	−0.0902 (19)	0.1143 (18)
C33P2	0.0592 (11)	−0.1827 (22)	0.1557 (23)
C34P2	0.0548 (15)	−0.2541 (26)	0.0809 (30)
O	0.1349 (5)	0.2537 (9)	−0.0467 (10)
F(1)	0.4236 (8)	0.1063 (19)	−0.0822 (16)
F(2)	0.4262 (12)	0.1383 (27)	0.0697 (22)
F(3)	0.4940 (12)	0.0376 (26)	−0.0824 (24)
F(4)	0.4928 (11)	0.0307 (21)	0.0826 (23)
F(5)	0.4181 (9)	0.0034 (20)	0.0263 (25)
F(6)	0.5020 (9)	0.1527 (15)	−0.0039 (19)

The scattering factors used were taken from ref 29. The correction for the real and imaginary parts of the atomic scattering was taken into account for the Pt, P, O, and Cl atoms.

Structural Studies of 2a. Crystals of **2a** have prismatic habit and are air stable. A suitable crystal of approximate dimensions 0.3 × 0.2 × 0.4 mm was mounted on a glass fiber for the data collection. Cell constants were obtained by least-squares fit of the 2θ values of 25 high-angle reflections ($15 \leq 2\theta \leq 20°$) using the centering routines in the PW 1100 diffractometer. Two standard reflections (2,3,3 and −2,−3,−3 measured every 2 h) were used to check the stability and orientation of the crystal and of the experimental conditions: no significant variation was detected.

An empirical absorption correction was applied by using the azimuthal ψ scans of reflections 311, 411, and 511. The structure was refined by using anisotropic temperature factors for Pt, Cl, O, and C atoms. The contribution of the hydrogen atoms in their calculated idealized positions (C–H = 0.98 Å; $B_{\mathrm{iso}} = 6.0$ Å^2) was taken into account but not refined. Upon convergence (no parameter shift greater than 0.3σ), the last difference Fourier showed no unusual features. Final positional parameters are listed in Table V.

Structural Studies of 11a. Some difficulties were found in obtaining a crystal of suitable quality for the X-ray analysis. A pale yellow crystal of approximate dimensions 0.3 × 0.1 × 0.05 mm was mounted on a glass fiber at a random orientation and used for the data collection. The space group ($P2_12_12_1$) and cell constants were obtained as above; crystal and data collection parameters are reported in Table IV. Three standard reflections (4,1,2, −4,1,2, −4,−1,−2) were checked every 3 h for stability of the crystal and of the experimental conditions. No significant variations were detected. Data were corrected for absorption by using the ψ scans of three reflections: −1,1,−2, −2,2,−4, and −3,3,−6. The structure was refined as above with the contribution of H atoms held fixed in their idealized position (C–H = 1.08 Å; $B_{\mathrm{iso}} = 7.0$ Å^2) and with anisotropic thermal factors for Pt, P, and Cl atoms. However the estimated standard deviations are somewhat large due probably to the disorder of the fluorine atoms. Upon convergence (no parameter shift greater than 0.5σ), the maximum electron densities in the cation were located around the Pt atom (about 0.7 e Å^{-3}). The high value of the fluorine thermal factors may be taken as evidence of some disorder around the P(3) atom. Four peaks (of approximately 0.5–0.7 e Å^{-3}) were found in the last Fourier difference map near atoms F(1), F(4), and F(5). Their inclusion in the refined model as fluorine atoms with partial occupancy factor gave positional parameters coincident with the existing ones and therefore were not retained. The handedness of the crystal was tested by refining the coordinates of the two enantiomorphs.[30] Those listed in Table VI gave the lower *R* factor.

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Registry No. **1a**, 105430-60-2; **2a**, 105430-59-9; **2c**, 105430-68-0; **3a**, 105430-61-3; **4a**, 105456-14-2; **5a**, 105456-15-3; **6a**, 105456-16-4; **7a**, 105456-17-5; **8a**, 105430-62-4; **9a**, 105430-63-5; **10a**, 105430-65-7; **11a**, 105430-67-9; **11c**, 105430-70-4; *cis*-$\mathrm{Pt(CO)_2Cl_2}$, 15020-32-3; $[\mathrm{Pt_2(C_2Pr_2)_4Cl_3}][\mathrm{Pt(CO)Cl_3}]$, 85025-21-4; $\mathrm{Pt(Ph_3)_2Cl_2}$, 10199-34-5; $[\mathrm{Pt_2(C_2Me_2)_4Cl_3}][\mathrm{Pt(CO)Cl_3}]$, 85025-18-9; $\mathrm{PPh_3}$, 603-35-0; $\mathrm{PBu_3}$, 998-40-3; 4-octyne, 1942-45-6; *p*-toluidine, 106-49-0; tetrapropylcyclopentadienone, 105430-58-8; tetrapropylcyclopentadienone (Diels–Alder derivative), 105456-13-1; piperidine, 110-89-4; 2-butyne, 503-17-3.

Supplementary Material Available: Tables of thermal factors, H-atom coordinates, and bond lengths and angles and torsion angles for compounds **2a** and **11a** (27 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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(29) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(30) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.