Organometallics 1992, *11*, 1187-1193 1187

Reactivity of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ toward $(C_6H_5)_2CN_2$. Synthesis and Molecular Structure of $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5)=N\text{-}N=(\eta^2\text{-}C_6H_5)C(C_6H_5)]$, an Ortho-Metalated Compound Containing an Unusual Intramolecular η^2-Arene–Pt Interaction

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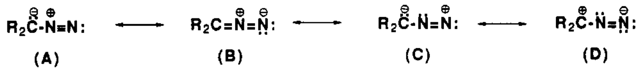
Treatment of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ (1) with $(C_6H_5)_2CN_2$ (2) affords *cis*-$Pt(C_6F_5)_2[(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2]$ (4), which can also be obtained by reacting 1 with $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$ (3). A possible structure of complex 4 is discussed both in terms of its spectroscopical features and its chemical behavior. 4 undergoes an ortho-metalation process by thermolysis either in solution or in the solid state, yielding $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5){=}N{-}N{=}(\eta^2\text{-}C_6H_5)C(C_6H_5)]$ (7), which has been structurally characterized by an X-ray diffraction study. 7 crystallizes in monoclinic space group $P2_1/n$ with a = 11.8359 (6) Å, b = 14.2561 (7) Å, c = 15.4549 (9) Å, β = 103.200(5)°; V = 2539 (1) Å^3, and Z = 4. One of the phenyl rings of the ortho-metalated benzophenone azine is η^2-coordinated to platinum, the whole ligand acting as tridentate. The η^2-aryl-Pt coordination, present in 7 and postulated in 4, is released by reaction of each compound with CO, thereby giving rise to $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5){=}N{-}N{=}C(C_6H_5)_2](CO)$ (8) and *cis*-$Pt(C_6F_5)_2[(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2](CO)$ (5), respectively.

Introduction

Diazo compounds, R_2CN_2, are among the most versatile reactants both in organic[1] and organometallic chemistry.[2] In their reactions with metal complexes they can act either as a source of the very reactive carbene fragment R_2C: or, without loss of molecular nitrogen, as a ligand.[3] These different pathways of reactivity, as well as the variety of coordination modes exhibited by the diazo group when attached to one or more metal centers must ultimately be ascribed to the "flexibility" of the resonance stabilized bond system (Scheme I) in addition to the nature of the metal center. For instance, diazo compounds are known to react with platinum complexes as typically shown in Scheme II: insertion of a carbene moiety into a Pt^{II}–X (X = halogen,[4,5] H[6]) or into a Pt^{I}–Pt^{I} bond[7] has been observed, while coupling of two diazo groups to give an η^2-coordinated azine takes place on a Pt(0) center.[4,8]

Scheme I



$$R_2\overset{\ominus\,\oplus}{C\text{-}N}{\equiv}N: \longleftrightarrow R_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}: \longleftrightarrow R_2\overset{\ominus}{C}\text{-}N{=}\overset{\oplus}{N}: \longleftrightarrow R_2\overset{\oplus}{C}\text{-}\ddot{N}{=}\overset{\ominus}{N}:$$

(A) (B) (C) (D)

In the course of our current research we have recently prepared *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ (1) (OC_4H_8 = tetrahydrofuran)[9] and studied its reactivity.[10] In this paper we study the reaction between 1 and $(C_6H_5)_2CN_2$ (2) because of the following reasons: (a) 1 contains two very labile OC_4H_8 ligands,[9] which has been pointed out as a prerequisite favoring the formation of carbene complexes,[2a] and (b) the M–C_6F_5 bonds are usually reluctant to undergo insertion reactions.[11]

Results and Discussion

(a) Reaction of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ (1) with Diphenyldiazomethane (2). When a diethyl ether solution of 1 is treated with an excess of 2, a colorless gas, presumably nitrogen, is evolved, and after 2 h of refluxing a yellow solid that we formulate as *cis*-$Pt(C_6F_5)_2[(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2]$ (4) can be isolated. The monomeric nature of this compound has been established on the basis of its molecular weight in solution (Table I; Scheme III).

The presence of coordinated benzophenone azine (3) in 4 has been confirmed by chemical means: (a) treatment of 4 with PPh_3 (1:2) in refluxing CH_2Cl_2 releases 3[12] with

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[1] Regitz, M.; Mass, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: New York, 1986. Patai, S., Ed. *The Chemistry of Diazonium and Diazo Groups*; John Wiley & Sons: Chichester, U.K., 1978.

[2] (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800. (b) Lappert, M. F.; Poland, J. S. *Adv. Organomet. Chem.* **1970**, *9*, 397.

[3] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283 and references cited therein. Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319.

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[9] Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912.

[10] Usón, R.; Forniés, J.; Tomás, M.; Menjón, B.; Carnicer, J.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 151 and references cited therein.

[11] Mukhedkar, A. J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3023. Cf. also: Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 2329 and references cited therein.

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Scheme II

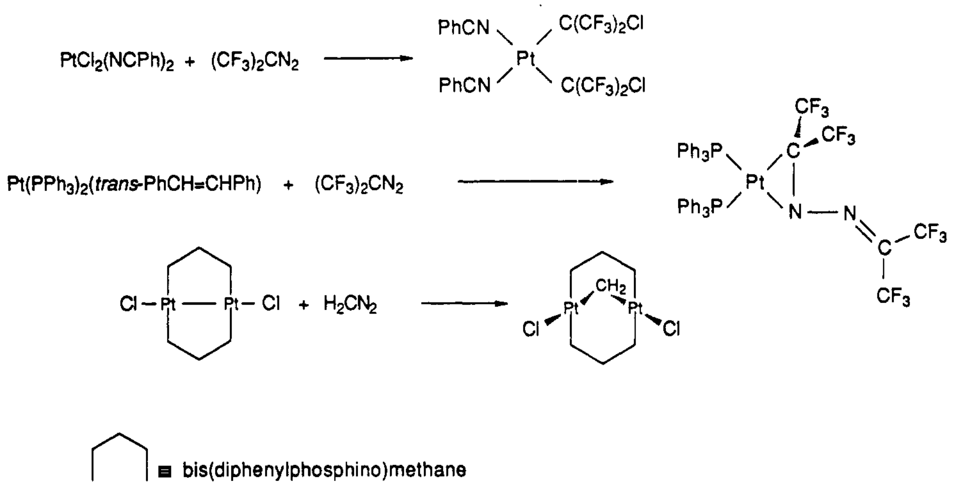

Table I. Analytical Results, Relevant IR Data, and Molecular Weight Values

complex	analysis,[a] % C	H	N	MW[a,b]	IR, cm^{-1} ν(CO)	X-sensitive vibration mode[c]
$C_{38}H_{20}F_{10}N_2Pt$ (4)	51.25 (51.30)	2.31 (2.27)	3.11 (3.15)	846.4 (889.6)		811 (s), 803 (sh), 800 (vs)
$C_{39}H_{20}F_{10}N_2OPt$ (5)	51.61 (51.04)	2.36 (2.20)	2.98 (3.05)	902.3 (917.7)	2110	809 (vs), 790 (vs)
$C_{32}H_{19}F_5N_2Pt$ (7)	53.26 (53.26)	3.07 (2.65)	3.88 (3.88)	735.5 (721.6)		796 (s)
$C_{33}H_{19}F_5N_2OPt$ (8)	53.07 (52.88)	2.76 (2.55)	3.47 (3.74)	759.7 (749.6)	2090	803 (s)

[a] Calculated values in parentheses. [b] Cryoscopic determination in $CHCl_3$ solution. [c] See: Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *26*, 288.

Table II. ^{1}H and ^{19}F NMR Data[a]

complex	^{19}F NMR *o*-F	*m*-F	*p*-F	^3J(Pt,*o*-F)	^{1}H NMR
4[b]	−118.5	−166.2	−163.3	408	7.2–7.6 (m, 19 H, aromatic H), 6.97 (tt, 1 H, ^3J(H,H) = 6.8, ^4J(H,H) = 2.0, 4″-H)
	−119.6	−166.8	−163.4	465	
5	−118.8[c]	−163.9	−160.3	405	7.2–8.1 (m, aromatic H)
		−164.3	−160.7		
7	−117.3	−165.3	−163.3	447	6.8–7.7 (m, 18 H, aromatic H), 6.50 (m, 1 H, ^3J(Pt,H) = 87.6, 3-H)
8	−120.8	−167.5	−164.6	437	6.9–7.6 (m, aromatic H), 6.69 (d, J = 7.2, ^3J(Pt,H) = 56, 3-H)
	−121.2			442	

[a] δ referenced to the nondeuterated residual solvent signal (^{1}H) or to $CFCl_3$ (^{19}F); J in Hz; unless otherwise stated $CDCl_3$ was used as solvent. [b] Solvent: CD_2Cl_2. [c] The *o*-F atoms resonate at the same frequency.

concomitant formation of *cis*-$Pt(C_6F_5)_2(PPh_3)_2$[14] (Scheme III); (b) **4** can also be obtained by reacting **1** with the stoichiometric amount of the preformed ligand **3**. This latter reaction proceeds in good yield and can therefore be considered as an alternative and more straightforward method of synthesizing **4** (Scheme III).

Differing from the trend shown by other Pt(II) complexes,[4-6] **1** reacts with $(C_6H_5)_2CN_2$, suffering no carbene insertion. Formation of metal-coordinated benzophenone azine (**3**) occurs instead, more resembling the behavior of zerovalent group 10 metal complexes toward diazoalkanes.[4,8] The mechanism of formation of **3** as well as its coordination mode must greatly differ in each case due to the different oxidation state of the metal centers. Thus, while perfluoroacetone azine coordinates the "$Pt^0(PPh_3)_2$" fragment through one of its C=N double bonds in a (*C,N*-η^2) fashion (see Scheme II),[8a] it seems sensible to assume that **3**, when attached to the more acidic "*cis*-$Pt^{II}(C_6F_5)_2$" moiety, is acting as a common nitrogen donor.

However, although **3** contains two N donor atoms, it should not be expected that both atoms will be coordinated to the same metal center because of the inadequate spatial disposition of the lone pairs on nitrogen; on the other hand, its acting as a binucleating bridging ligand[15] can be excluded on the basis of molecular weight measurements in chloroform solutions, so that only one of the N atoms should be coordinated to the metal center and some further interaction must arise between **3** and the platinum center for the latter to achieve tetracoordination. A simple way to accomplish this is by interacting with the π-system of a phenyl group of **3**, which could act as an η^2-alkene-like ligand (Scheme IV). Such a coordination mode would fix one of the phenyl rings in a close proximity to one C_6F_5 group, which could possibly affect the magnetic environment of the corresponding *p*-H (4″-H). In fact, the ^{1}H NMR spectrum of **4** shows an upfield signal (δ 6.97 ppm, tt, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 2.0 Hz) well apart from the aromatic resonances (δ 7.2–7.6 ppm), thus supporting our structural proposal. No further effects due to the

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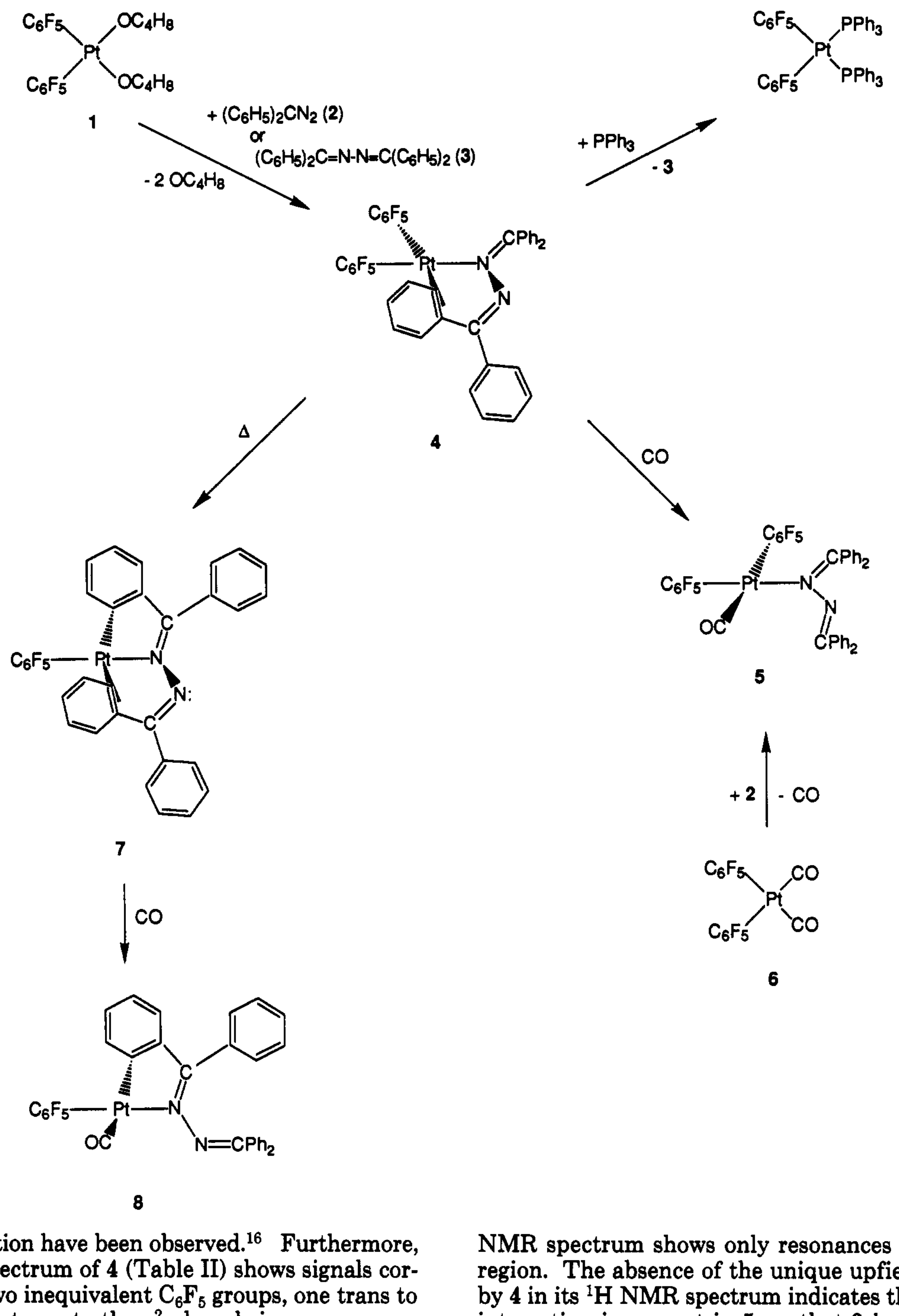
(12) Identified by C, H, and N analysis, melting point, and IR and mass spectroscopy, compared with an authentic sample prepared as in ref 13.

(13) Taipale, K. A. *Ber. Dtsch. Chem. Ges.* **1930**, *63B*, 243.

(14) Rosevear, D. T.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5275.

(15) Complexes $[Pd(2\text{-}C_6H_4)\text{—}C(R)\text{=}N\text{—}NPh)L]_2$ (R = Me, Ph; L = $P(OMe)_3$, 4-methylpyridine) are dimeric as reported in: Espinet, P.; Garcia, G.; Herrero, F. J.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1989**, *28*, 4207.

Scheme III



η^2-aryl coordination have been observed.[16] Furthermore, the ^{19}F NMR spectrum of 4 (Table II) shows signals corresponding to two inequivalent C_6F_5 groups, one trans to N and the other trans to the η^2-phenyl ring.

Treatment of 4 with CO does not liberate 3, in contrast to the behavior displayed by this compound in its reaction with PPh_3. In this case, coordination of one molecule of CO per platinum center occurs, giving rise to 5 (Scheme III), which can be isolated as a white crystalline solid. Its IR spectrum shows an absorption at 2110 cm^{-1}, assignable to $\nu(CO)$, in accordance with the values observed for other similar monocarbonyl complexes.[17] Its ^{19}F NMR spectrum shows signals due to two inequivalent C_6F_5 groups. Its ^1H NMR spectrum shows only resonances in the aromatic region. The absence of the unique upfield signal shown by 4 in its ^1H NMR spectrum indicates that no η^2-phenyl interaction is present in 5, so that 3 is acting as a conventional monodentate N-donor ligand.

The ability of CO to break the proposed η^2-phenyl interaction on 4 seems to indicate that this η^2-interaction is very labile even though assisted by the chelate effect of ligand 3.[18] On the other hand, 4 remains unaltered on reaction with either CO_2 or nonacidic acetylenes RC≡CR (R = Ph, $SiMe_3$).

Complex 5 can be obtained by reacting *cis*-$Pt(C_6F_5)_2(CO)_2$ (6) with diphenyldiazomethane (2) (Scheme III).[18]

To account for the formation of coordinated benzophenone azine (3) starting from diphenyldiazomethane (2)

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[16] (a) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812. (b) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Ossor, H.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2975. (c) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26* 508. (d) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Ibid.* **1987**, *26*, 1169.

[17] Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1986**, *5*, 1581.

[18] It is noteworthy to compare this behavior with that displayed by bis(diphenylphosphino)methane or 2,2'-bipyridine, typical chelating ligands, which are able to displace the two CO groups on *cis*-$Pt(C_6F_5)_2(CO)_2$ in a nonreversible process.[17]

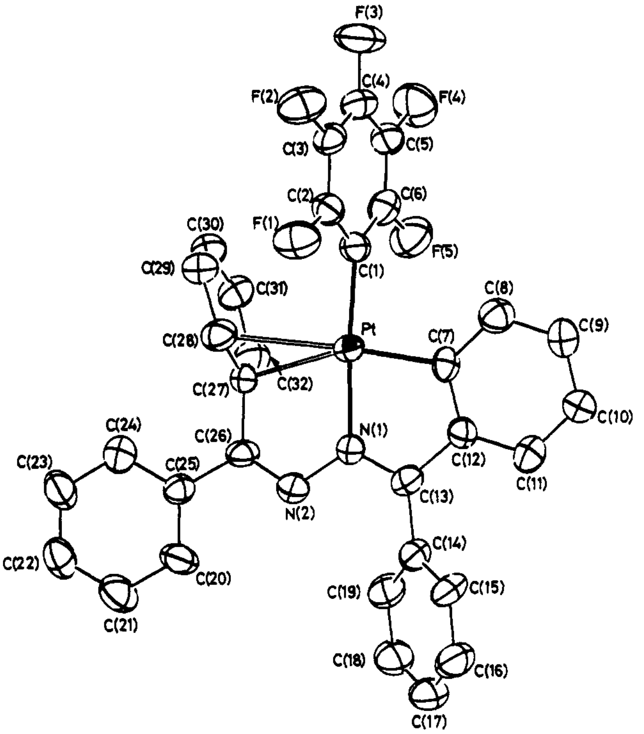

Figure 1. ORTEP drawing of complex 7. Hydrogen atoms have been omitted for clarity.

and either 1 or 6, we propose as plausible the following reaction pathway (Scheme IV): (1) one labile group L on the metal substrate is replaced by diphenyldiazomethane in its resonant form **2A**; (2) the coordination through the basic carbon atom enhances the cationic character or the diazo group, then leaving as a dinitrogen molecule;[19] (3) the generated carbene complex (**10**)[20] undergoes nucleophilic attack at the carbene carbon[21] by a further diazo molecule, now in its resonant form **2B**. This process, which can be regarded as a 1,2-dipolar addition, yields directly **5** with L = CO. When L = OC_4H_8, subsequent intramolecular substitution should render the final complex **4**.

We propose **4** to have the structure depicted in Scheme IV on the basis of its spectroscopic data and chemical behavior. The definitive confirmation of this proposal can, however, be obtained only from an X-ray diffraction analysis. Unfortunately, we have till now not been able to grow suitable crystals for such a study.

(b) Thermolysis of 4. Toluene solutions of **4**, when refluxed for 1 h, render **7** in good yield as a red, crystalline compound (Scheme III), which has been characterized by elemental analysis, spectroscopic methods (IR, ^1H, and ^{19}F NMR), and X-ray diffraction analysis.

An ORTEP drawing of the molecular structure of **7** is shown in Figure 1. General crystallographic information is collected in Table III. Final atomic positional parameters are listed in Table IV. Selected interatomic distances and angles are listed in Table V. The platinum atom is coordinated to a C_6F_5 group and to the ligand 1-*o*-phenylen-1,4,4-triphenyl-2,3-diaza-1,3-butadiene which is acting as a tridentate ligand. A part of this ligand is coordinated via a nitrogen (N1) donor bond and a carbon (sp^2)-σ-bond of the ortho-position of a phenyl ring resulting

Table III. Summary of X-ray Diffraction Data for $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5)=N-N=(\eta^2\text{-}C_6H_5)C(C_6H_5)]$ (7)

formula	$C_{32}H_{19}F_5N_2Pt$
fw	721
space group	$P2_1/n$
cell params[a]	
a, Å	11.8359 (6)
b, Å	14.2561 (7)
c, Å	15.4549 (9)
β, deg	103.200 (5)
V, Å^3	2539 (1)
Z	4
cryst dimens, mm	0.42 × 0.23 × 0.23
temp, °C	20
λ(Mo Kα radiation), Å	0.71069
μ, cm^{-1}	53.5
corrn for abs	7 Ψ scans
transm coeff	0.2251–0.3307
data colln	$\omega-2\theta$
2*θ* range, deg	4–50 (+14,+16,±18)
no. of reflns collcd	4903
no.of ind reflns	4262
agreement between equiv reflns	*R* = 0.0159
no. of unique data $I > 3\sigma(I)$	3560
final no. of variables	361

[a] From 24 reflections plus their Friedel-opposite reciprocal lattice points in the range $27° < 2\theta < 31°$.

Table IV. Fractional Atomic Coordinates ($\times10^4$) and Their Estimated Standard Deviations for $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5)=N-N=(\eta^2\text{-}C_6H_5)C(C_6H_5)]$ (7)

atom	*x*	*y*	*z*
Pt	2555 (1)	519 (1)	721 (1)
F1	4135 (4)	659 (3)	2698 (3)
F2	3622 (5)	679 (4)	4285 (3)
F3	1410 (6)	578 (3)	4439 (4)
F4	−319 (5)	510 (3)	2976 (4)
F5	113 (4)	467 (3)	1347 (3)
N1	2949 (5)	591 (3)	−479 (4)
N2	3535 (5)	−117 (4)	−815 (3)
C1	2157 (7)	566 (4)	1921 (5)
C2	3009 (6)	623 (4)	2717 (5)
C3	2749 (7)	627 (4)	3553 (5)
C4	1666 (7)	598 (5)	3645 (5)
C5	774 (7)	555 (5)	2889 (6)
C6	1034 (6)	532 (5)	2065 (5)
C7	1983 (5)	1805 (4)	349 (4)
C8	1443 (6)	2437 (5)	823 (5)
C9	1089 (7)	3323 (5)	437 (5)
C10	1235 (7)	3559 (5)	−407 (5)
C11	1745 (6)	2931 (5)	−886 (5)
C12	2148 (6)	2058 (5)	−491 (4)
C13	2692 (6)	1352 (5)	−957 (4)
C14	2925 (6)	1486 (5)	−1852 (4)
C15	3468 (7)	2273 (5)	−2069 (4)
C16	3668 (7)	2366 (6)	−2928 (5)
C17	3315 (7)	1704 (7)	−3551 (5)
C18	2739 (8)	881 (7)	−3331 (5)
C19	2557 (8)	769 (6)	−2508 (5)
C20	4480 (7)	−1644 (5)	−1485 (5)
C21	5060 (7)	−2421 (5)	−1771 (5)
C22	5395 (7)	−3175 (5)	−1208 (6)
C23	5128 (7)	−3201 (5)	−396 (6)
C24	4528 (6)	−2455 (5)	−106 (5)
C25	4223 (5)	−1673 (4)	−648 (4)
C26	3593 (6)	−878 (5)	−364 (4)
C27	3083 (6)	−1005 (4)	447 (4)
C28	3809 (6)	−958 (6)	1288 (4)
C29	3435 (7)	−1381 (6)	2028 (5)
C30	2374 (7)	−1783 (6)	1886 (5)
C31	1606 (7)	−1807 (5)	1048 (5)
C32	1987 (6)	−1438 (6)	308 (5)

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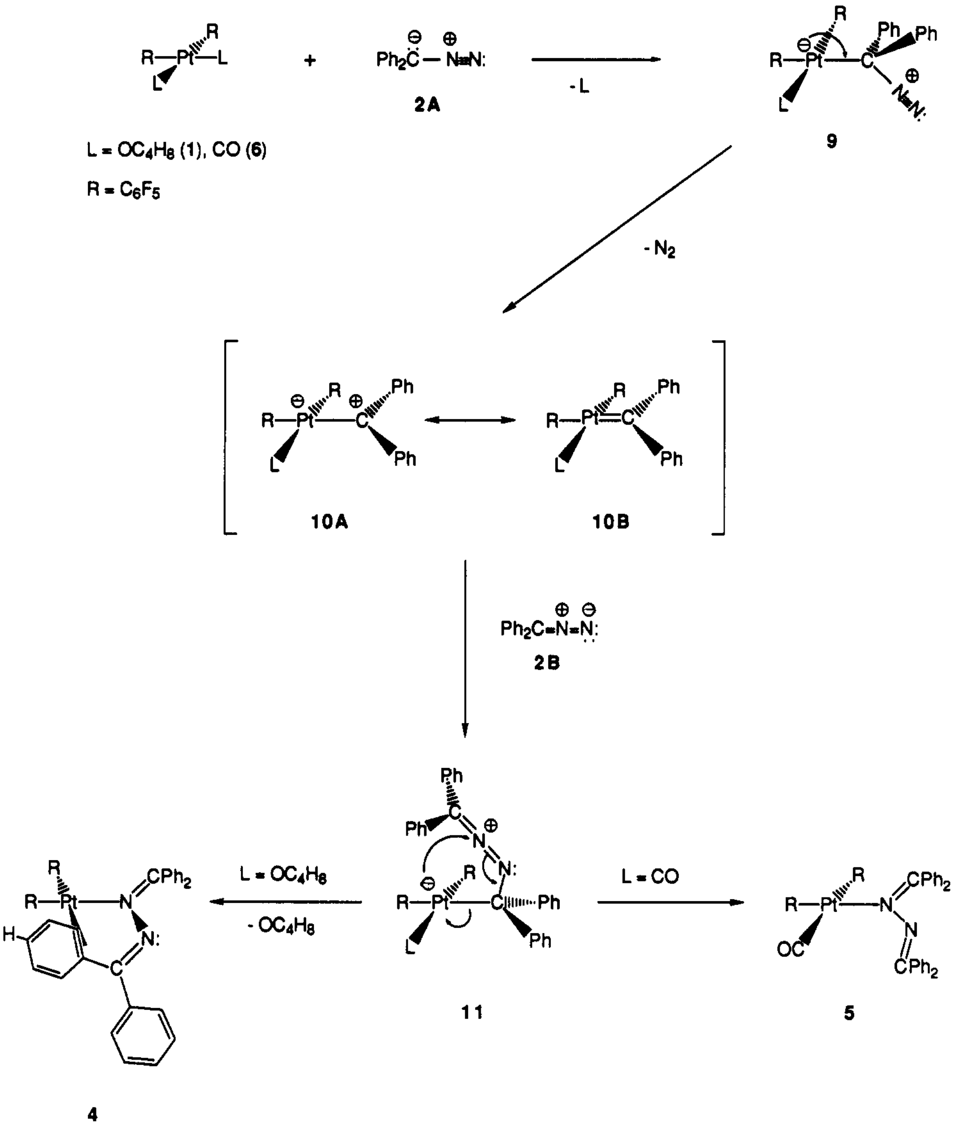
[19] Steps 1 and 2 of the proposed reaction pathway are relevant to the accepted mechanism for diazoalkane dimerization: Abelt, C. J.; Pleier, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 1795.

[20] Note that, when L = CO, the proposed intermediate **10** does not suffer carbonyl insertion into the carbene fragment. Conversely, this is supposed to be a key step in the formation of $(C_6H_5)_2C=C=O$ by reacting $(C_6H_5)_2CN_2$ (**2**) with $Ni(CO)_4$: Rüchardt, C.; Schrauzer, G. N. *Chem. Ber.* **1960**, *93*, 1840.

[21] The electron-withdrawing substituents on platinum greatly favor the electrophilic character of the carbene carbon.

Scheme IV



in a planar five-membered ring. The carbon atoms of the ortho-phenylene ring are virtually located in the same plane.

The Pt–C7 (1.993 (6) Å) distance falls in the lower range for usual Pt–C(sp^2) bond lengths and also the Pt–N1 (2.016 (6) Å) distance is slightly shorter than normally found in Schiff-base complexes of Pt.[22] Finally, one of the phenyl rings is interacting through the C27–C28 atoms in a η^2-fashion with the platinum center, thus completing its tetracoordination. The Pt–C27 (2.327 (6) Å) and Pt–C28 (2.610 (7) Å) distances are different. Disimilarities in the M–C distances have also been reported for other complexes in which a η^2-arene–M bond has been invoked.[16d,23] The Pt–C distances are much longer than those observed in standard η^2-alkene complexes of platinum.[24] Long Pd–C distances have also been found in $[NC_9H_6CH_2C(CF_3){=}C(CF_3)]Pd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6OCH_3)]$ which

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5){=}N{-}N{=}(\eta^2\text{-}C_6H_5)C(C_6H_5)]$ **(7)**

	Central Core		
Pt–C1	2.017 (8)	C1–Pt–C7	95.7 (3)
Pt–C7	1.993 (6)	C7–Pt–N1	79.8 (2)
Pt–N1	2.016 (6)	C1–Pt–N1	175.2 (2)
Pt–C27	2.327 (6)	C27–Pt–C28	32.0 (2)
Pt–C28	2.610 (7)	C27–C28–Pt	62.7 (4)
		C27–Pt–C7	153.4 (2)
		C28–Pt–C7	165.6 (2)
	Ortho-Metalated Ring		
C7–C8	1.403 (9)	C7–C8–C9	118.5 (6)
C8–C9	1.419 (10)	C8–C9–C10	121.4 (7)
C9–C10	1.395 (10)	C9–C10–C11	120.4 (7)
C10–C11	1.386 (10)	C10–C11–C12	118.8 (7)
C11–C12	1.420 (9)	C11–C12–C7	121.2 (6)
C12–C7	1.404 (9)	C12–C7–C8	119.6 (6)
	η^2-Aryl Group		
C27–C28	1.386 (9)	C27–C28–C29	119.0 (7)
C28–C29	1.448 (9)	C28–C29–C30	119.2 (7)
C29–C30	1.351 (11)	C29–C30–C31	122.9 (7)
C30–C31	1.403 (11)	C30–C31–C32	118.4 (7)
C31–C32	1.422 (10)	C31–C32–C27	119.3 (6)
C32–C27	1.409 (10)	C32–C27–C28	121.1 (6)

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contains a η^2-aryl–Pd interaction.[16d]

Moreover, no significant structural differences between the non-metalated uncoordinated phenyl rings in **7** and the coordinated one can be observed (Table V); the ring remains almost planar and the C–C bond distances within it do not follow the alternating sequence long–short–long, thus pointing to a small loss of aromaticity in the ring upon coordination. All these structural features suggest that the η^2-phenyl–Pt interaction is weak in nature and favored by the possibility of the ortho-metalated benzophenone azine to act as a tridentate ligand, thus completing the tetracoordination of the platinum center. It is noteworthy that, in spite of the documented ability of C_6F_5 groups to act as bridging ligands[25] and the presence of a noncoordinated N donor atom in **7**, the platinum center does not reach tetracoordination through polynuclear association but through a η^2-phenyl–Pt interaction, as suggested to be present in **4**. Although often proposed as intermediates in homogeneous hydrogenation reactions of arenes catalyzed by transition-metal complexes[26] as well as in C-(sp^2)–H activation pocesses—including the well-known ortho-metalation reactions[27]—η^2-metal-coordinated arenes are most common for metal centers with a $d^{10}s^0$ electronic configuration.[28] Continued interest in materializing this coordination mode at metal centers of other d^x ($x < 10$) electronic configurations has led to the identification and isolation of a number of complexes,[29] of which, to our knowledge, the following have been structurally characterized: $[\{Os(NH_3)_5\}_2(\mu\text{-pyrene})][O_3SCF_3]_4$,[23a] dicarbonyl(2–4-$\eta^3$-8-(trimethylsiloxy)-8-(1′,2′-η^2-phenyl)bicyclo[3.2.1]octenyl)(triphenylphosphine)manganese (I),[23b] $(PhHCPz'_2)Mo(CO)_3$, (Pz′ = 3,5-dimethylpyrazol-1-yl),[23c] $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$,[23d] $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$,[23e] $(C_5H_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)$,[23f] $[NC_9H_6CH_2C(CF_3){=}C(CF_3)]Pd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$,[16d] and $[(C_5Me_5)Re(CO)_2]_2(\mu\text{-}\eta^2{:}\eta^{2'}\text{-}C_6H_6)$.[23g]

The process undergone by **4** on thermolysis (Scheme III) implies the ortho-metalation of one of the phenyl rings of coordinated benzophenone azine (**3**)[30] with concomitant elimination of a C_6F_5 group, probably leaving as—stoichiometrically required—C_6F_5H. This kind of cyclometalation reaction in metal complexes containing phenyl-substituted ligands is especially favored when, as it is the case in **4**, a five-membered ring can be formed. On the other hand, the facility of **4** to undergo the ortho-metalation process could be a consequence of the η^2-phenyl–Pt interaction.

Finally, as observed for complex **4**, the η^2-phenyl–Pt interaction in **7** is released in the presence of a ligand. Its reaction with carbon monoxide renders complex **8** (Scheme III) which contains a terminal carbonyl group [ν(CO) 2090 cm^{-1}]. However, as for **4**, **7** does not react with CO_2 or nonacidic acetylenes RC≡CR (R = Ph, $SiMe_3$).

Experimental Section

C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000–200 cm^{-1}). ^{1}H and ^{19}F NMR spectra were recorded on either a Varian XL-200 or a Unity-300 spectrometer. Thermogravimetry was performed on a Perkin-Elmer TGS-2 apparatus equipped with a System 4 microprocessor controller at a heating rate of 10 K min^{-1} under nitrogen. Molecular weights were determined in $CHCl_3$ solution with a Knauer digital osmometer. Literature methods were used to prepare $(C_6H_5)_2CN_2$,[31] $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$,[13] *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$, and *cis*-$Pt(C_6F_5)_2(CO)_2$.[9]

***cis*-$Pt(C_6F_5)_2[(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2]$ (4).** (a) By adding **2** (0.17 g, 0.87 mmol) to a colorless solution of **1** (0.2 g, 0.29 mmol) in diethyl ether (20 mL), a rapid gas evolution was observed as the solution turned deep red. After 2-h reflux, the solution became yellow. Then, the solvent was evaporated to dryness and, when the resulting residue was treated with *n*-hexane, a white solid was obtained (**4**, 0.15 g, 76% yield), which can be recrystallized from diethyl ether/*n*-hexane.

(b) A diethyl ether (20 mL) solution containing equimolar quantities of **1** (0.2 g, 0.29 mmol) and **3** (0.1 g, 0.29 mmol) was refluxed for 2 h. By workup of the resulting yellow solution as in the previous section, 0.16 g of **4** were obtained (62% yield).

***cis*-$Pt(C_6F_5)_2[(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2](CO)$ (5).** (a) Passing a slow stream of CO through a yellow solution of **4** (70 mg, 0.056 mmol) in CH_2Cl_2 (15 mL) caused it to pale. After 20 min the solvent was evaporated to dryness. The resulting residue, when treated with *n*-hexane, gave rise to 0.04 g of a white solid (**5**, 58% yield).

(b) To a solution of **6** (0.23 g, 0.39 mmol) in CH_2Cl_2 (25 mL) was added **2** (0.24 g, 1.23 mmol), and the reaction mixture was refluxed for 1 h, after which time the solvent was evaporated to dryness. When the resulting residue was treated with *n*-hexane, 0.19 g of **5** were obtained (46% yield).

$Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5){=}N{-}N{=}(\eta^2\text{-}C_6H_5)C(C_6H_5)]$ (7). When a yellow solution of **4** (0.2 g, 0.16 mmol) was refluxed in toluene (50 mL) for 1 h, its color turned red. Afterward, the solvent was evaporated to dryness and the resulting residue was extracted with diethyl ether and filtered off. Subsequent evaporation of the filtrate yielded a red solid, which was washed with *n*-hexane and collected (**7**, 0.13 g, 65% yield).

$Pt(C_6F_5)[(2\text{-}C_6H_4)C(C_6H_5){=}N{-}N{=}C(C_6H_5)_2](CO)$ (8). Passing a slow stream of CO through a red solution of **7** (0.2 g, 0.18 mmol) in toluene (15 mL) caused it to become yellow. After 30 min the solution was evaporated to dryness. The resulting residue, when treated with *n*-hexane, gave rise to a cream solid, which was filtered off and dried (**8**, 0.12 g, 60% yield).

X-ray Structure Analysis of 7. X-ray diffraction data (Table III) were collected on a Siemens/Stoe AED2 diffractometer with profile-fitted intensities;[32] no decay was observed. The platinum atom was found by Patterson methods and all remaining nonhydrogen atoms were located by successive difference Fourier syntheses. All of the atoms were refined anisotropically. The

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refinement converged at $R = 0.035$ and $R_w = 0.043$ (weighting scheme: $w^{-1} = \sigma^2(F_o) + 0.0023F_o^2$). There was only one peak higher than 1 e/Å^3 in the final difference map (2.3 e/Å^3) which was located at 0.83 Å from the heavy atom. All calculations were performed using SHELX-76.[33]

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Supplementary Material Available: Tables of anisotropic thermal parameters and complete distances and angles (2 pages); a listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Unprecedented Coordination of a Si–Cl Bond to a Transition Metal: Synthesis and Structure of [*rac*-C_2H_4(indenyl)$_2$Zr{CH(SiMe$_2$Cl)(SiMe$_3$)}][$Al_2Cl_{6.5}Me_{0.5}$] Formed by Reversible Si–C Bond Activation

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Reaction of Cp′$_2$Zr{CH(SiMe$_3$)$_2$}Cl with a 2-fold excess of AlCl$_3$ affords the novel Si–C bond activation products [Cp′$_2$Zr{CH(SiMe$_2$Cl)(SiMe$_3$)}][Al$_2$Cl$_n$Me$_{7-n}$] (Cp′$_2$ = *rac*-C$_2$H$_4$(indenyl)$_2$ (**1**), (C$_5$H$_5$)$_2$ (**2**)); the Lewis acid adducts Cp′$_2$Zr{CH(SiMe$_3$)$_2$}Cl·AlCl$_3$ are obtained with 1 equiv of AlCl$_3$. In contrast, Cp′$_2$Zr(CH$_2$SiMe$_3$)Cl (Cp′$_2$ = *rac*-C$_2$H$_4$(indenyl)$_2$, (C$_5$Me$_5$)$_2$) undergoes rapid alkyl–chloride exchange with AlCl$_3$, giving Cp′$_2$ZrCl$_2$·(Me$_3$SiCH$_2$)AlCl$_2$. The structure of [*rac*-C$_2$H$_4$(indenyl)$_2$Zr{CH(SiMe$_2$Cl)(SiMe$_3$)}][Al$_2$Cl$_{6.5}$Me$_{0.5}$] (**1**) has been determined by X-ray crystallography. Crystal data: $C_{26.5}H_{33.5}Al_2Cl_{7.5}Si_2Zr$, M_r 819.3, monoclinic, $P2_1/n$, $a = 9.419$ (2) Å, $b = 23.134$ (5) Å, $c = 17.418$ (4) Å, $Z = 4$, final $R = 0.053$ for 5215 "observed" reflections. The unusual chelating alkyl ligand shows the first example of Si–Cl bond coordination to a transition metal (Zr–Cl = 2.573 (1) Å; Si–Cl = 2.266 (2) Å; Zr–Cl–Si = 80.4 (1)°). The Si–C bond activation reaction leading to **1** is reversible, as shown by formation of *rac*-C$_2$H$_4$(indenyl)$_2$Zr{CH(SiMe$_3$)$_2$}Cl on reaction of **1** with a 2-fold excess of AlMe$_3$. Sterically and electronically saturated **1** is inert toward unsaturated substrates. Treatment of **1** with Lewis bases affords *rac*-C$_2$H$_4$(indenyl)$_2$Zr{η^1-CH(SiMe$_2$Cl)(SiMe$_3$)}Cl (**3**).

Introduction

The hypothesis that a cationic complex, [Cp′$_2$MR]$^+$, is the active species in alkene polymerization catalysts, based on group 4 metallocenes with alkylaluminoxane[1] or alkylaluminum halide[2] cocatalysts, has recently led to the synthesis of well-characterized d^0 cocatalyst-free cationic model complexes.[3,4] A number of Lewis base adducts, [Cp′$_2$MR(L)]$^+$,[3] have been prepared, but more electrophilic alkylmetallocene cations, more closely related to the active site in the two-component catalysts, are frequently less stable and have been less extensively studied.[4] Direct in situ study of the active two-component catalysts has been attempted using NMR,[5] UV,[6] and XPS[7] techniques but is hindered by the complexity and dynamic nature of the

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