Four-Membered 1,8-Naphthalenediyl Transition Metallacycles

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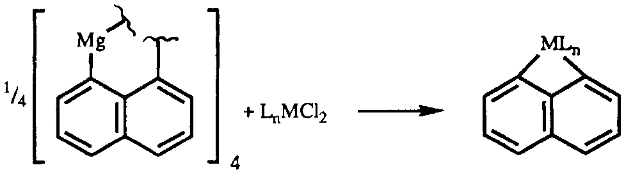
Five 1,8-naphthalenediyl transition metal compounds **2** were prepared by treating either 1,8-naphthalenediylmagnesium (**1**) or 1,8-dilithionaphthalene with the appropriate transition metal dichloride L_nMCl_2: $L_nM = Cp_2Ti$ (**2a**), $(PEt_3)_2Pt$ (**2b**), Cp^*PPh_3Rh (**2c**), Cp^*PPh_3Ir (**2d**), or Cp^*_2Zr (**2e**). The resulting metallacycles were characterized by NMR and mass spectrometry. X-ray crystal structure analyses were performed for (1,8-naphthalenediyl)titanocene (**2a**) and (1,8-naphthalenediyl)bis(triethylphosphane)platinum (**2b**). Despite the strain induced by the four-membered metal-containing rings, the naphthalene units show remarkably small distortions.

Metallacyclobutanes form a class of compounds that has received considerable interest, mainly because of their (presumed or proven) intermediacy in several catalytic processes, such as olefin metathesis[1]. Many synthetic approaches have been developed to prepare metallacyclobutanes. In our group, di-Grignard reagents are the starting-point, and it has been shown that 1,3-di-Grignard reagents are excellent synthons for the preparation of metallacyclobutanes[2].

Recently, (1,8-naphthalenediyl)magnesium (**1**) has been prepared and structurally characterized[3]. The 1,3-relationship between the organomagnesium functions called for an investigation of the suitability of **1** as a reagent for the formation of four-membered metallacycles (Scheme 1).

Scheme 1



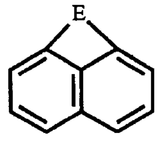
1

2	L_nM
a	Cp_2Ti
b	$(Et_3P)_2Pt$
c	$Cp^*(Ph_3P)Rh$
d	$Cp^*(Ph_3P)Ir$
e	Cp^*_2Zr

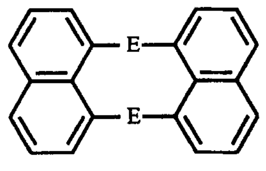
Cp = cyclopentadienyl
Cp* = pentamethylcyclopentadienyl

Special interest in the resulting 1,8-naphthalenediyl transition metal compounds **2** stems from the obvious strain that is imposed on the metal-carbon bonds; the small endocyclic valence angles in the four-membered ring of **2** cause large deviations for the carbon-centered angles from the ideal 120°. For that reason, the formation of dimeric compounds **4**, i.e. compounds containing a 1,5-dimetallacyclooctane unit, could not be excluded beforehand. In Scheme 2, known representatives of both monomeric (**3**) and dimeric (**4**) species are listed. The only known transition metal compound is dimeric **4b**; in view of the preferred linear coordination geometry of mercury(II), this is not surprising[10].

Scheme 2



3	E	ref.
a	CH_2	[4]
b	CHBr	[5] (X-ray)
c	$SiMe_2$	[6]
d	$SiEt_2$	[6]
e	S	[7]
f	SO_2	[8] (X-ray)



4	E	ref.
a	$SnMe_2$	[9] (X-ray)
b	Hg	[10] (X-ray)

From the X-ray crystal structure analyses of **3b** and **3f** the severe strain in these compounds can be deduced; the naphthalene moieties are strongly distorted to accommodate the four-membered ring. Although bond lengths as well as angles deviate from the ideal values, no significant deviations from planarity have been observed. In the analogous transition metal compounds **2** (Scheme 1), which are the topic of the present investigation, the metals have tetra-

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hedral or square-planar coordination spheres; they are expected to be less strained because of the metals involved tend to form relatively small C−M−C bond angles. X-ray structures of metallacyclobutanes with these metals show values around 70°[11].

Results and Discussion

Synthesis of Four-Membered 1,8-Naphthalenediyl Transition Metallacycles

The synthesis of (1,8-naphthalenediyl)titanocene (**2a**), (1,8-naphthalenediyl)bis(triethylphosphane)platinum (**2b**), (1,8-naphthalenediyl)(pentamethylcyclopentadienyl)(triphenylphosphane)rhodium (**2c**), and (1,8-naphthalenediyl)(pentamethylcyclopentadienyl)(triphenylphosphane)iridium (**2d**) was straightforward according to Scheme 1. A solution of **1** in THF or toluene was added to the transition metal dichloride at −20°C, and the mixture was stirred at 5°C or room temperature until the reaction was complete (1 to 12 hours). The product was isolated by evaporation of the solvent followed by extraction of the residue with heptane or toluene; the insoluble magnesium salts were removed by filtration. Attempts to prepare (1,8-naphthalenediyl)zirconocene in an analogous fashion failed. Though zirconocene dichloride did react with **1** to give two zirconocene products as evidenced by two ^{1}H-NMR signals assignable to cyclopentadienyl groups (in a 2:3 ratio), the compounds could not be separated and characterized with the techniques available in a sealed glass system. Zirconium compound **2e** was obtained from the reaction of $Cp^*_2ZrCl_2$ with 1,8-dilithionaphthalene in diethyl ether; after evaporation of the reaction mixture to dryness, the pure compound was isolated by extraction with hexane.

NMR and Mass Spectroscopy

The compounds were identified by NMR spectroscopy of the available nuclei. The ^{1}H-NMR spectrum of **2a** showed an ABC pattern for the aromatic protons and a singlet for the cyclopentadienyl protons. The ^{13}C-NMR spectrum of **2a** revealed two remarkable chemical shifts for quaternary carbons: one strongly deshielded (δ = 202.2), assigned to the carbon atoms bound directly to titanium (C-1 and C-8), in analogy to the assignment in diphenyltitanocene (δC-1 = 192.9)[12]. The other one is relatively shielded (δ = 92.5) and tentatively assigned to C-9. The shielding of C-9 may be explained by a directed shielding effect of the Cp_2Ti unit due to the very short distance of titanium to C-9. This has also been observed for β-carbon atoms in titanacyclobutanes as well as for protons attached to them[2b,2d,13].

Compound **2b** was characterized by ^{1}H-, ^{13}C-, ^{31}P-, and ^{195}Pt-NMR spectroscopy. The ^{195}Pt-NMR spectrum showed a triplet, indicating the presence of a platinum atom coordinated to two equivalent phosphorus atoms; this was confirmed by the ^{31}P-NMR spectrum in which one signal with ^{195}Pt satellites was found. The observed ^1J(P-Pt) of 2058 Hz is larger than those normally found for *cis*-diarylbis(trialkylphosphane)platinum(II) compounds (1700−1800 Hz)[14]. Similar large couplings have been reported for 1,1-bis(trialkylphosphane)-1,2-dihydro-1-platina(II)cyclobutabenzenes [1797−2058 Hz; e.g. 2009 and 1845 Hz for the bis(triethylphosphane) derivative]. The ^{1}H-NMR spectrum showed the expected signals, although the ABC pattern in the aromatic region was not completely resolved. The ^{13}C-NMR spectrum of **2b** was quite complex due to the presence of couplings with ^{1}H, ^{31}P, and ^{195}Pt nuclei. Decoupling experiments permitted the assignment of the peaks and the evaluation of the coupling constants (see Experimental). Not all of the Pt-C coupling constants could be determined due to the low intensity of some of the ^{195}Pt satellites. Signals from quaternary carbon atoms were found at δ = 170.4, 128.5, and 127.0. The signal at δ = 170.4 was initially assigned to C-1 and C-8 on the basis of its deshielded value [cf. *cis*-diphenylbis(tributylphosphane)platinum (**5**); δ(C-1) = 163.9[14]]. However, the evaluation of the (P-C) coupling constants showed that only the signal at δ = 128.5 had two different (P-C) couplings (55 and 5 Hz). This signal therefore must arise from C-1 and C-8, these being the only quaternary carbon atoms with different relationships to both P nuclei (*cis* and *trans*). Analogous couplings were observed in the spectrum of **5** [coupling constants of the *ipso*-carbons: $^2J(\text{P-C})_{trans}$ = 112, and $^2J(\text{P-C})_{cis}$ = 14 Hz[14]].

cis-$Ph_2Pt(PBu_3)_2$ **5**

Carbon atoms C-9 and C-10 should experience equal couplings from both the P nuclei because of their symmetrical orientation, as is the case with the signals at δ = 170.4 and 127.0. The assignment of the deshielded shifts to either C-9 or C-10 is not unambiguous; the magnitude of the coupling constants in **2b** cannot simply be compared to those in **5** in view of the special bonding situation in **2b**. If, however, one assumes that the ^3J(Pt-C) is larger than the ^2J(Pt-C) like in **5** (65 and 33 Hz, respectively[14]), then the more deshielded signal must be assigned to C-10!

Compounds **2c** and **2d** were characterized by ^{1}H- and ^{31}P-NMR spectroscopy. Due to the presence of the triphenylphosphane ligand, the aromatic regions in the ^{1}H-NMR spectrum were very complex. A definite assignment of the naphthalene protons was not possible, but the presence of one doublet for the Cp* methyl protons [^4J(P-H) ≈ 2 Hz] is indicative of the presence of only one compound. This could also be concluded from the ^{31}P-NMR spectra which showed a doublet for **2c** [$^1J(^{103}\text{Rh-P})$ = 165.5 Hz] and a singlet for **2d**. Further structural characterization was derived from mass spectrometry (vide infra).

The ^{1}H-NMR spectrum of **2e** was well resolved. The ABC pattern in the aromatic region, indicative for a 1,8-disubstituted naphthalene, and the single Cp* signal were in accord with the structure of **2e**.

All compounds were subjected to a mass spectrometric investigation (see Experimental). In none of the mass spectra was found an indication of a dimeric compound (such as **4** in Scheme 2). The molecular ion cluster of the monomer always formed the base peak in the spectrum.

X-Ray Crystal Structure Determinations

A definite proof of the structure of **2** was found in the X-ray crystal structures of **2a** and **2b**. Their molecular structures are depicted in Figures 1 and 2. Apart from the cyclopentadienyl and phosphane ligands, the molecules are essentially flat, i.e. the metal atom lies in the plane of the naphthalene system. The analogy between the structures is obvious, although the coordination modes of the two metals are quite different. The inherently smaller angles in square-planar-coordinated Pt as compared to pseudotetrahedrally coordinated Ti are reflected in the endocyclic C−M−C bond angles of 66.57(15) and 71.2(2)° in **2b** and **2a**, respectively (cf. Cp$_2$TiPh$_2$, C−M−C 97.3°[15]), in spite of the fact that the Pt−C bond [$\bar{d}$ = 2.094(4) Å] is only insignificantly longer than the Ti−C bond [$\bar{d}$ = 2.089(7) Å]! The other endocyclic angles are different as well, resulting in a slightly more pronounced elongation of the four-membered ring along the metal−C9 axis is **2b**. As a result, the metal···C9 distance is larger in **2b** [2.580(4) Å] than in **2a** [2.442(7) Å]. The latter value is considerably shorter than the sum of the van der Waals radii of titanium and carbon (2.90 Å). As such, this might have indicated a bonding interaction between the two atoms; however, on the basis of both qualitative MO considerations and a theoretical calculation[16] there is no orbital of appropriate symmetry at C9, so that there can be no bonding between Ti and C9. This makes the two short bonds Ti−C1 and Ti−C8 all the more remarkable (vide infra).

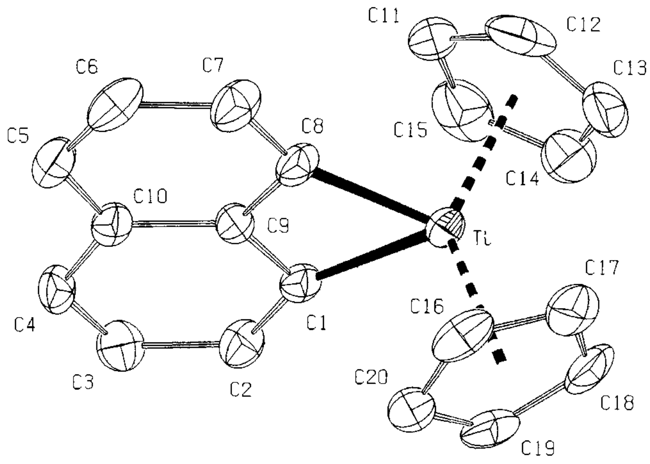

Figure 1. ORTEP drawing of **2a** (drawn at 30% probability level) with atom labeling. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Ti−C1 2.083(7), Ti−C8 2.094(7), Ti···C9 2.442(7), C1−C2 1.363(8), C1−C9 1.423(8), C7−C8 1.366(9), C8−C9 1.428(8), C9−C10 1.430(7); C1−Ti−C8 71.2(2), Ti−C1−C9 86.1(3), C2−C1−C9 117.8(5), Ti−C8−C9 85.6(3), C7−C8−C9 117.7(5), C1−C9−C8 117.1(4), C1−C9−C10 121.9(4), C8−C9−C10 121.0(5)

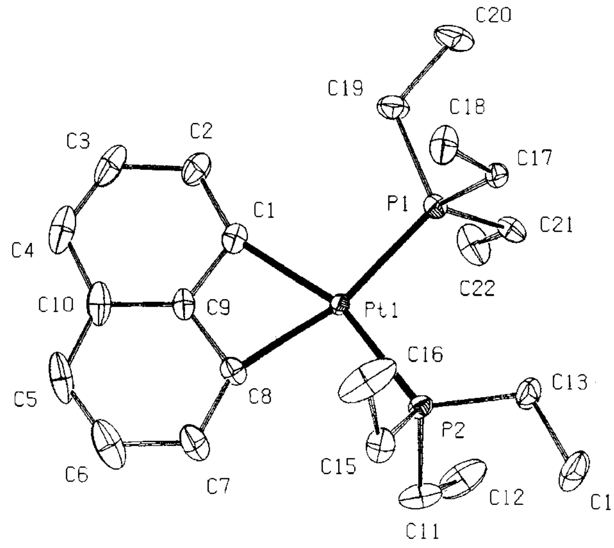

Figure 2. ORTEP drawing of **2b** (drawn at 50% probability level) with atom labeling. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pt1−P1 2.2788(11), Pt1−P2 2.2868(10), Pt1−C1 2.100(4), Pt1−C8 2.087(4), Pt1···C9 2.580(4), C1−C2 1.365(6), C1−C9 1.425(6), C7−C8 1.381(6), C8−C9 1.414(6), C9−C10 1.406(6); P1−Pt1−P2 100.18(4), P1−Pt1−C8 166.45(11), P2−Pt1−C1 159.62(11), P2−Pt1−C8 93.25(11), C1−Pt1−C8 66.57(15), Pt1−C1−C2 151.9(3), Pt1−C1−C9 92.0(3), C2−C1−C9 116.0(4), Pt1−C8−C7 150.8(3), Pt1−C8−C9 92.9(3), C7−C8−C9 116.2(4), C1−C9−C8 108.1(4), C1−C9−C10 125.7(4), C8−C9−C10 126.1(4)

The distortion of the naphthalene moiety of **2b** is larger than in **2a**. Actually, the distortion in **2b** resembles that in **3b**[5] and **3f**[8], but is not quite as severe. The way in which the strain is divided over the molecule is different for all four compounds. This is probably caused by several factors including the length and the polarity of the bonds from the atom bridging between C1 and C8. Empirically, one observes that the degree of distortion of the naphthalene moiety [as measured e.g. for the angle C1−C9−C8 in **3b** 99°, **3f** 106°, **2b** 108.1(4)°, **2a** 117.1(4)°] increases roughly with the electronegativity difference between the bridging atom and carbon [electronegativities for C 2.5, S 2.5 (SO$_2$ < 2.5), Pt 2.2, Ti 1.5[17]]; in the same direction, the ionic contribution to these bonds increases. We suggest that due to the increased ionic character of the Ti−C bonds, their directional dependence decreases. This is in line with the angle at the *peri*-carbons C1 and C8 [e.g. M−C1−C9 is larger for **2b** (average 92.5(3)°) than for **2a** (average 85.9(3)°]; i.e. because of the more covalent character of the C−Pt bond this angle in **2b** tends to stay closer to the sp^2 value of 120°C at the expense of the angle at C9 [108.1(4)°] and Pt [66.57(15)°], whereas the directional dependence of the more polarized C−Ti bond is less pronounced. As a consequence, less strain is imposed on the naphthalene system in **2a**, allowing it to more closely adhere to its original, "natural" geometry. The concept of a relatively high ionic contribution to the Ti−C bonds may also help to understand the unexpected phenomenon that the Ti−C bond is unusually short [$\bar{d}$ = 2.089(7) Å; cf. $\bar{d}$(Ti−C(phenyl)) = 2.272(14) Å[15]] in spite of the presumably severe nonbonded interaction between Ti and C9 (vide supra). The (formal!) Cp$_2$Ti^{2+} cation interacts with two "carbanionic" carbons (a formal dianion!) in close proximity; this will increase the Coulomb attraction, expecially as the dissipation of the negative charge in the naphthalene system will be reduced in comparison with two independent phenyl groups. In contrast, the Pt−C bond lengths in **2b** [$\bar{d}$ = 2.094(4) Å], where such ionic effects will be much less important, are slightly longer than those in "normal" Pt-phenyl complexes [cf. *trans*-diphenylbis(triphenylphosphane)Pt(II): $\bar{d}$ = 2.079 Å[18]; *cis*-bis(2-nitrophenyl)bis(triphenylphosphane)Pt(II): $\bar{d}$ = 2.061 Å[19]; *cis*-bis(2-methoxyphenyl)bis(triphenylphosphane)-Pt(II): $\bar{d}$ = 2.033 Å[20].

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Experimental

Unless stated otherwise, all reactions were carried out in fully sealed and evacuated glass systems. Solvents were dried with a sodium potassium alloy before use. Cp_2TiCl_2 and Cp_2ZrCl_2 were commercially available; $Cp^*_2ZrCl_2$ was a gift from Koninklijke/Shell Laboratorium Amsterdam. Synthesis of 1,8-dilithionaphthalene · TMEDA[21] was achieved according to the procedure described by Brandsma et al.[21a]. 1,8-Diiodonaphthalene[22], *cis*-$(PEt_3)_2PtCl_2$[23], $Cp^*(PPh_3)RhCl_2$[24], and $Cp^*(PPh_3)IrCl_2$[24] were prepared according to literature procedures. – NMR: Bruker WM 250. – MS: Finnigan MAT 90.

(1,8-Naphthalenediyl)titanocene (**2a**): A solution of **1**[3b] in toluene (0.29 mmol in 10 ml) was added to Cp_2TiCl_2 (0.0726 g, 0.29 mmol) at –20°C. The reaction mixture was allowed to warm to 5°C; after 3 h a yellow-orange solution was obtained. At room temp. the solution was separated from the precipitated magnesium chloride by careful decantation and filtration. Further purification was achieved by crystallization from hexane at –80°C to give yellow needles of **2a**. – ^1H NMR (250 MHz, C_6D_6, ref. C_6D_5H δ = 7.17): δ = 7.63–7.58 (m, 4H, 2,4,5,7-H), 7.40 [dd, ^3J(H-H) = 8.0, ^3J(H-H) = 6.5 Hz, 2H, 3,6-H], 5.43 (s, 10H, Cp-H). – ^{13}C NMR (62.9 MHz, [D$_8$]dioxane, ref. [D$_7$]dioxane δ = 66.5): δ = 202.2 (br. s, C-1,8), 132.4 (br. s, C-9 or C-10), 128.5 [dd, ^1J(C-H) = 159, ^3J(C-H) = 8 Hz, C-2,7], 126.5 [d, ^1J(C-H) = 159 Hz, C-3,6], 124.3 [dt, ^1J(C-H) = 158.0, 2 × ^3J(C-H) ≈ 5 Hz, C-4,5], 112.3 [dd, ^1J(C-H) = 174.0, ^3J(C-H) = 6 Hz, Cp], 92.3 (br. s, C-9,10). – MS (EI), *m/z* (%): 306 (6), 305 (19), 304 (72) [M$^+$], 303 (21), 302 (50), 301 (6), 300 (5), 278 (6), 237 (11), 211 (14), 190 (10), 189 (19), 151 (11), 128 (100), 113 (28). Molecular ion cluster, relative intensities calcd. for $C_{20}H_{16}Ti$: 306 (11), 305 (29), 304 (100), 303 (12) 302 (6). – $C_{20}H_{16}Ti$ (304.0): calcd. C 78.95, H 5.30, Ti 15.74; found C 77.40, H 5.21. – $C_{20}H_{16}{}^{48}Ti$: calcd. 304.0732, found 304.0670 (MS, EI).

(1,8-Naphthalenediyl)bis(triethylphosphane)platinum(II) (**2b**): A solution of **1** (5 ml, 0.030 M) in THF was added to $(PEt_3)_2PtCl_2$ (0.0753 g, 0.15 mmol) at room temp. After 1 h all $(PEt_3)_2PtCl_2$ had disappeared, and a yellow solution was obtained. The solvent was distilled off and 20 ml of heptane was added to the residue. The precipitated magnesium chloride was removed by filtration. Crystallization from heptane or toluene by cooling a saturated solution gave light brown plate-shaped crystals of **2b**. – ^1H NMR (250 MHz, C_6D_6, ref. C_6D_5H δ = 7.17): δ = 7.80–7.83 (m, 2H), 7.51-7.63 (m, 4H), 1.70 [qd, ^3J(H-H) = 7.8, ^2J(P-H) = 7.8 Hz, 6H, PCH$_2$], 0.90 [td, ^3J(H-H) = 7.9, ^3J(P-H) = 15.8 Hz, 9H, CH$_3$]. – ^{13}C-NMR (62.9 MHz, CDCl$_3$, ref. CDCl$_3$ δ = 77.0): δ = 170.4 [^3J(Pt-C) = 125 Hz, C-10], 128.5 [^2J(P-C) = 55, ^2J(P-C) = 5 Hz, C-1,8], 127.0 [^2J(Pt-C) = 38 Hz, C-9], 125.3 [^1J(C-H) = 156, 2 × ^4J(P-C) ≈ 2, ^3J(Pt-C) = 38 Hz, C-3,6], 119.6 [^1J(C-H) = 155, ^3J(C-H) = 8, ^2J(Pt-C) = 28, 2 × ^3J(P-C) = 5 Hz, C-2,7], 118.9 [^1J(C-H) = 160, 2 × ^3J(C-H) ≈ 6, ^4J(P-C) = 6 Hz, C-4,5], 18.2 [^1J(C-H) = 129, ^1J(P-C) = 31, ^2J(P-C) = 27 Hz, PCH$_2$], 8.65 [^1J(C-H) = 123, ^2J(P-C) ≈ 0, ^3J(P-C) = 22 Hz, CH$_3$]. – ^{31}P NMR (101.3 MHz, CDCl$_3$, external ref. 85% H_3PO_4 δ = 0): δ = 9.0 [s, ^1J(Pt-P) = 2058 Hz]. – ^{195}Pt NMR (53.77 MHz, CDCl$_3$, external ref. K_2PtCl_6 in D_2O δ = 0): δ = –4028.9 (t, ^1J(Pt-P) = 2058 Hz). – MS (EI), *m/z* (%): 560 (17), 559 (20), 558 (91), 557 (100) [M$^+$], 556 (88), 529 (15), 499 (36), 470 (20), 431 (16), 403 (38), 374 (54), 347 (25), 243 (27), 128 (41). – MS (FD), *m/z* (%): 560 (11), 559 (7), 558 (85), 557 (100) [M$^{+\cdot}$], 556 (70), 72 (59) [THF$^{+\cdot}$]. Relative intensities in the molecular ion cluster calculated for $C_{22}H_{36}P_2Pt$: 560 (19), 559 (17), 558 (82), 557 (100) [M$^{+\cdot}$], 556 (79). – $C_{22}H_{36}P_2Pt$ (557.3): calcd. C 47.39, H 6.51, P 11.11, Pt 34.99; found C 47.39, H 6.58, P 11.1, Pt 35.1. – $C_{22}P_{36}P_2{}^{195}Pt$: calcd. 557.1941, found 557.1869 (MS, EI).

(1,8-Naphthalenediyl)(pentamethylcyclopentadienyl)(triphenylphosphane)rhodium (**2c**): A solution of **1** in THF (9 ml, 0.030 M) was added to $Cp^*(PPh_3)RhCl_2$ (0.154 g , 0.27 mmol) at –20°C. After 1 h the reaction mixture was warmed to 5°C and stirred overnight. The THF was removed by distillation and the residue extracted with 10 ml of toluene. The toluene was evaporated from the extract, and the residue was washed twice with 10 ml of pentane resulting in solid **2c**.

^1H NMR (250 MHz, C_6D_6, ref. C_6D_5H δ = 7.17): δ = 7.46–7.43 [m (≈dd), 2H, 2,7-H?], 7.39–7.30 (m, 6H, Ph-2,5-H), 7.22–7.20 (m, 4H, 3,4,5,6-H?), 6.96–6.92 (m, 9H, Ph-3,4,5-H), 1.53 [d, ^4J(P-H) = 2.4 Hz, Cp-H]. – ^{31}P NMR (101.3 MHz, C_6D_6, external ref. 85% H_3PO_4 δ = 0): δ = 54.3 [d, ^1J(Rh-P) = 166 Hz]. – MS (EI), *m/z* (%): 628 (7), 627 (39), 626 (100) [M$^{+\cdot}$], 491 (16), 441 (58), 387 (19), 313 (15), 286 (17), 262 (35), 252 (33), 210 (12), 183 (20). – Molecular ion cluster, calcd. for $C_{38}H_{36}PRh$: 628 (9), 627 (43), 626 (100). – $C_{38}H_{36}P^{103}Rh$: calcd. 626.1596; found: 626.1615 (MS, EI).

(1,8-Naphthalenediyl)(pentamethylcyclopentadienyl)(triphenylphosphane)iridium (**2d**): A solution of **1** in THF (5 ml, 0.030 M) was added to $Cp^*(PPh_3)IrCl_2$ (0.099 g, 0.15 mmol) at –20°C. After 1 h the reaction mixture was warmed to room temp. and stirred overnight. The THF was removed by distillation, and the residue was extracted with 20 ml of toluene. The toluene was evaporated from the extract resulting in solid **2d**. – ^1H NMR (250 MHz, C_6D_6, ref. C_6D_5H δ = 7.17): δ = 7.84–7.80 [m (≈dd), 2H, 2,7-H?], 7.50–6.93 (complex multiplett), 1.54 [d, ^4J(P-H) = 1.8 Hz, Cp-H]. – ^{31}P NMR (101.3 MHz, C_6D_6, external ref. 85% H_3PO_4 δ = 0): δ = 17.3 (s). – MS (EI), *m/z* (%): 718 (7), 717 (36), 716 (100) [M$^{+\cdot}$], 715 (30), 714 (72), 712 (8), 626 (12), 590 (51), 511 (18), 454 (19), 387 (15), 358 (12), 323 (29), 262 (41), 183 (42), 128 (16). – Relative intensities in the molecular ion cluster, calcd. for $C_{38}H_{36}IrP$: 718 (8), 717 (41), 716 (100), 715 (24), 714 (57). – $C_{38}H_{36}{}^{193}IrP$: calcd. 716.2188; found 716.2202 (MS, EI).

Reaction of **1** *with* Cp_2ZrCl_2: A solution of **1** in toluene (8 ml 0.037 M) was added to Cp_2ZrCl_2 (0.0864 g, 0.296 mmol) at 5°C. After stirring for 2 h the reaction mixture was allowed to warm to room temp. and stirred overnight. The resulting yellow solution was separated from magnesium halides by filtration; the solvent was removed by distillation, and the residue was examined by ^1H-NMR spectroscopy. Two signals originating from Cp groups were visible, suggesting the presence of two zirconocene derivatives. Attempts to separate these by extraction with hexane or crystallization failed. – ^1H-NMR (250 MHz, C_6D_6, ref. C_6D_5H δ = 7.17): δ = 7.73–7.17 (complex multiplet), 5.91 (s, Cp-H), 5.65 (s, Cp-H).

(1,8-Naphthalenediyl)bis(pentamethylcyclopentadienyl)zirconium (**2e**): In a Schlenk-type glass apparatus under argon 1,8-dilithio-

naphthalene · $(TMEDA)_n$,[21a] (0.140 g, 0.55 mmol) was suspended in 10 ml of diethyl ether and the suspension cooled to −70°C; THF (1 ml) and $Cp^*_2ZrCl_2$ (0.225 g, 0.52 mmol) were added subsequently. After 15 min the cooling bath was removed, and the mixture was allowed to warm slowly to room temp. After stirring overnight a yellow-orange solution containing a white precipitate was obtained. In order to remove the lithium halide the solvent was distilled off, and the residue was extracted twice with 20 ml of *n*-hexane. The solvent was evaporated from the combined extracts leaving 0.208 g of a yellow solid (**2e**, 82%). – ^1H NMR (250 MHz, C_6D_6, ref. C_6D_5H $\delta = 7.17$): $\delta = 7.75$ [dd, $^3J(H-H) = 8.4$, $^4J(H-H) = 0.9$ Hz, 2H, 2,7-H], 7.70 [dd, $^3J(H-H) = 6.5$, $^4J(H-H) = 1.1$ Hz, 2H, 4,5-H], 7.40 [dd, $^3J(H-H) = 8.4$, $^3J(H-H) = 6.5$ Hz, 2H, 3,4-H], 1.52 (s, 30H, Cp*-H). – MS (EI), *m/z* (%): 532 (4), 504 (23), 491 (7), 490 (13), 489 (10), 488 (20), 487 (22), 486 (40) $[M^+]$, 485 (9), 484 (15), 469 (44), 432 (52), 395 (42), 377 (89), 295 (100), 252 (94), 135 (68), 128 (76), 119 (91). – Relative intensities in the molecular ion cluster, calcd. for $C_{30}H_{36}Zr$: 491 (12), 490 (36), 489 (13), 488 (46), 487 (55), 486 (100). Signals at *m/z* values larger than those of the molecular ion cluster originate from reaction products of **2e** with water [e.g. **2e** · H_2O and **2e** · $(H_2O)_2$] during the preparation of the sample. – $C_{30}H_{36}{}^{90}Zr$: calcd. 486.1864; found 486.1833 (MS, EI).

Structure Determination and Refinement of **2a**: X-Ray data were collected with an Enraf-Nonius CAD4F diffractometer for an orange needle-shaped crystal sealed in a Lindemann glass capillary. Numerical details are collected in Table 1. Data were corrected for Lp, no decay was observed. The structure was solved by direct methods (SHELXS86/TREF[26] and refined in *F* by full-matrix least-squares technique with SHELX76[29]. Hydrogen atoms were taken into account at calculated positions with two common U_{iso} and C−H = 0.98 Å riding on their carrier atoms.

Table 1. Crystal data and details of the structure determination of **2a** and **2b**

	a) Crystal data	
Compound	2a	2b
Mol. Wt.	304.23	557.55
Formula	$C_{20}H_{16}Ti$	$C_{22}H_{36}P_2Pt$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a, b, c Å	8.202(1), 14.78(3), 12.402(1)	9.9019(10), 12.8393(10), 17.782(2)
β (°)	95.96(1)	
V (Å^3)	1495(3)	2260.7(4)
Z	4	4
D_{calc} (g cm^{-3})	1.352	1.638
F(000) (electrons)	632	1104
μ (cm^{-1})	5.5	64.1
Crystal size	0.08x0.10x1.75	0.12x0.60x0.50
	b) Data collection	
Temperature (K)	295	100
θ_{min}, θ_{max}	1.37, 27.5	1.15, 27.50
Radiation	MoKα(Zr-filtered), 0.71073 Å	MoKα(Zr-filtered), 0.71073 Å
Scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (°)	$0.80 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
Hor. and vert. aperture (mm)	3.0, 5.0	3.0, 5.0
Dist. cryst. to detector (mm)	173	173
Reference reflections	1 0 -1, 0 3 -1, 1 1 0	-3 0 1, -3,-2 0, 0 3 2
Data set	h -10:10; k 0:19; l -16:16	h -12:0; k -16:16; l 0:23
Total data	8710	7865
Total unique data	3445	5085
Observed data	1646 [$I > 2.5\sigma(I)$]	4880 [$I > 2.5\sigma(I)$]
	c) Refinement	
No. of refined refls./pars.	1646, 192	4880,247
Weighting scheme	$w = [\sigma^2(F) + 0.00016F^2]^{-1}$	$w = [\sigma^2(F) + 0.000179F^2]^{-1}$
Final R, wR, S	0.065, 0.053, 1.24	0.0216, 0.0264, 1.70
$(\Delta/\sigma)_{av}$ and max. in final cycle	0.04, 0.3	0.0124, 0.232
Min. and max. resd. dens. e/Å^3	-0.50, 0.64	-0.92, 1.20 (Near Pt)

Structure Determination and Refinement of **2b**: A brownish plate-shaped crystal was glued on top of a glass fiber and transferred immediately to the cold nitrogen stream of an Enraf-Nonius CAD4F diffractometer for data collection at 100 K. Unit cell parameters were determined by a least-squares treatment of the SET4 setting angles of 25 reflections with $14.0 < \Theta < 18.0°$. Unit cell parameters were checked for the presence of higher lattice symmetry[25]. Data were corrected for Lp, for absorption (DIFABS[31]; correction range 0.879−1.609) and for a linear decay of 2.1% of the intensity control reflections during the 114 hours of X-ray exposure time. The structure was solved with standard Patterson methods (SHELXS86[26]) and subsequent difference Fourier analyses. Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced into calculated positions [C−H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms with common isotropic thermal parameters [$U = 0.043(7), 0.034(4), 0.047(4)$ Å^2 for CH, CH_2, and CH_3, groups respectively]. Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.0216$, $wR = 0.0264$, $w = 1/[\sigma^2(F) + 0.000179F^2]$. The absolute structure was checked by refinement with opposite anomalous dispersion factors (-if") resulting in $R = 0.0507$, $wR = 0.0664$. Crystal data and numerical details of the structure determination are given in Table 1.

Neutral atom scattering factors for **2a** and **2b** were taken from ref.[27] and corrected for anomalous dispersion[28]. All calculations for **2a** and **2b** were performed with SHELX76[29] and PLATON[30] (geometrical calculations and illustrations) on a DEC-5000 cluster[32].

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