

Rigid *trans*-spanning triptycene-based ligands: How flexible they can be?

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Received 13 September 2006; received in revised form 29 September 2006; accepted 29 September 2006

Available online 14 October 2006

Abstract

trans-[1,8-Bis(diisopropylphosphino)triptycene]nickel (II) dichloride, *trans*-[1,8-bis(diisopropylphosphino)triptycene]carbonylrhodium (I) chloride and *cis*-[1,8-bis(diisopropylphosphino)triptycene]platinum (II) dichloride have been prepared and fully characterized in order to evaluate the coordination diversity of triptycene-based bidentate ligands. Their structural features and coordination preferences were studied and compared to the previously reported palladium complexes. The comparative structural analysis revealed that 1,8-bis(diisopropylphosphino)triptycene is able to access a variety of bite angles and to stabilize metal centers in different geometries. In addition, intramolecular weak C–H···Cl–Pt hydrogen bonding interactions which stabilize [1,8-bis(diisopropylphosphino)triptycene]platinum (II) dichloride in a constrained *cis* form are discussed.

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Keywords: *trans*-Spanning; Triptycene; Intramolecular hydrogen bond; Transition metal complexes; Bidentate ligands

1. Introduction

Complexation of transition metal centers by bidentate ligands in *trans* fashion has attracted much attention since the 1961 when Issleib and Hohlfeld synthesized the first *trans*-spanned square planar nickel complex using the flexible bis(dicyclohexylphosphino)pentane as a ligand [1]. Thereafter, a number of flexible and rigid chelates exhibiting analogous chelating preferences were prepared, characterized and studied [2]. Notably, the great challenge in design and synthesis of new bidentate ligands capable of spanning across a transition metal center at the angle of ca. 180° is mainly reasoned by their remarkable structural features: unusual geometries of the metal center may be adopted, unique steric and/or electronic (including asymmetric) environment may be created, and a crib-like shelter for the transition metal may be attained. All these considerations motivated prospects toward novel catalysis. Indeed, the recently introduced new *trans*-chelating ligands families such as Xantphos [3], SPANphos [4], TRAP [5], BISBI [6] and *m*-terphenyl-based diphosphines [7] demon-

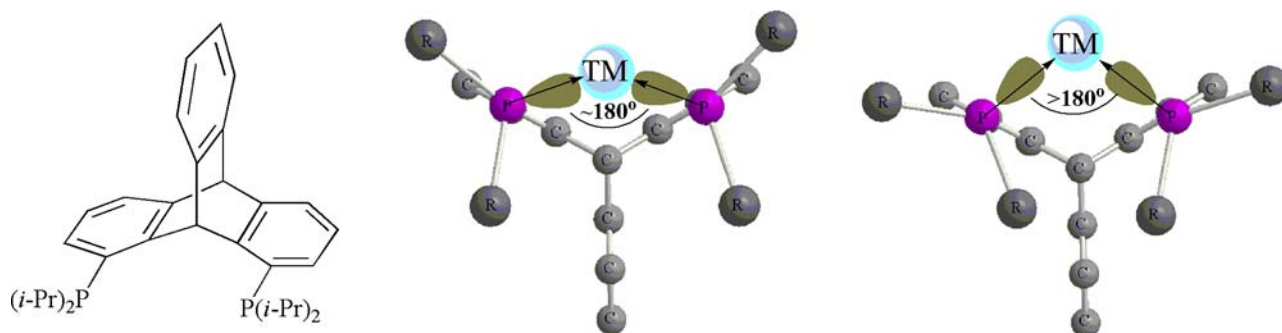
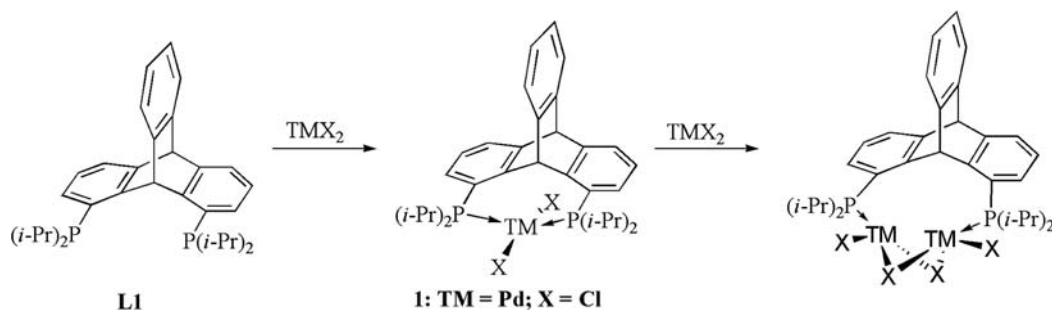
strated exceptional catalytic activity in a variety of organic transformations. On the other hand, *trans*-spanned structures found multiple applications in supramolecular [8] and bioinorganic [9] chemistry.

Recently, we communicated on the synthesis and characterization of a new representative of a potentially *trans*-chelating bidentate ligands class based on the triptycene scaffold (Fig. 1, left) [10]. According to our initial hypothesis, the bent shape of its skeleton along with a possible rotation of the phosphine donors around the C–P bonds will result in the “self-adjustable” ligand capable to adopt a variety of geometries (Fig. 1, right).

Indeed, the initial investigation of their coordination chemistry disclosed a very unusual behavior [10,11]. Inter alia, we found that depending on the reaction conditions 1,8-bis(diisopropylphosphino)triptycene (**L1**) is able to bind palladium and rhodium centers in either chelating mode – forming truly *trans*-spanned structures, or binucleating mode – forming unusual quasi-closed bimetallic complexes possessing a bent $\text{TM}_2(\mu\text{-Cl}_2)$ core (Scheme 1).

On the other hand, the previously reported monometallic palladium complexes (such as **1**, Scheme 1) demonstrated very promising catalytic activity in some selected cross-coupling reactions (Suzuki coupling and

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Fig. 1. Possible coordination modes of **1** in transition metal complexes.Scheme 1. Possible coordination modes of **L1**.

cyanation of aryl halides) [10,12] implying that not only observed *trans*-spanned species but also *cis*-chelated intermediates (necessary in cross-coupling chemistry) formed over the course the catalytic cycles. However, our previous attempts to synthesize and structurally characterize transition metal complexes that featured bite angles lower than 160° failed.

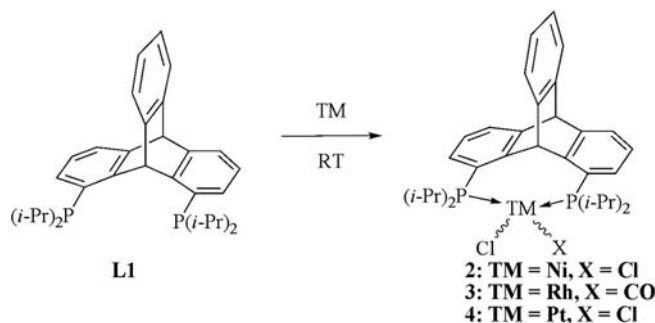
Therefore, in this report we wish to readdress the following issues: (i) Is the ligand indeed “self-tunable” and can stabilize transition metals of different size and identity? (ii) Is the ligand able to coordinate transition metals in a factual *cis*-fashion despite the considerable nonbonding P...P distance and apparent rigidity of the triptycene platform?

In order to estimate experimentally the degree of flexibility of the triptycene-based ligands, we prepared and fully characterized [1,8-bis(diisopropylphosphino)triptycene] nickel (II) dichloride (**2**), [1,8-bis(diisopropylphosphino)triptycene]carbonylrhodium (I) chloride (**3**) [13] and [1,8-bis(diisopropylphosphino)triptycene]platinum (II) dichloride (**4**). Their structural features and coordination preferences were studied and compared to the previously reported palladium complexes [10].

2. Results and discussion

2.1. Synthesis of d^8 transition metal complexes

All complexes have been prepared according to Scheme 2. The Ni(II) complex **2** was obtained via the reaction of **L1**

Scheme 2. Synthesis of **2**, **3** and **4**.

with the stoichiometric amount of the freshly prepared (1,2-dimethoxyethane)dichloronickel in acetonitrile. The reaction mixture changed color immediately from pale pink to deep blue and was stirred at room temperature for 24 h. The product was readily isolated as a pure material in 83% yield and showed the proper elemental analysis that was consistent with a 1:1 chelate compound.

The ^1H NMR of **2** showed very broad peaks which could not be correctly assigned. The signals broadening suggested the paramagnetic behavior of the complex that could be consistent with a tetrahedral-like geometry at the nickel center.

Synthesis of **3** was accomplished by reacting one equivalent of **L1** with 1/2 an equivalent of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in chloroform. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3**, as expected, displayed a doublet with the resonance frequency

of 39.16 ppm and Rh–P coupling constant of 127 Hz. The magnitude of the coupling constant is indicative of *trans*-coordinated rhodium diphosphine compounds [14]. ^1H NMR spectrum also strengthened the *trans* geometry of the product – signal ascribed to a central methine hydrogen appears at a very low field (9.11 ppm) suggesting a close proximity of the hydrogen to the metal center. Accounting a conjectural “self-tunability” of the ligand (Fig. 1), such an arrangement is only possible if donors are coordinated to the metal center in *trans* fashion.

Four sets of doublet of doublets in the region δ 1.1–1.6 ppm and two separate multiplets in the region δ 2.7–3.1 ppm appear in ^1H NMR spectrum due to the methyl and, respectively, methine protons on the four isopropyl groups. This pattern suggests C_s symmetry of **3** in solution.

The analogous Pt(II) complex **4** was obtained upon stirring 1:1 mixture of *cis*-PtCl₂(CH₃CN)₂ precursor and **L1** in acetonitrile at room temperature for 16 h. $^{31}\text{P}\{^1\text{H}\}$ NMR measurements indicated the formation of two products (in ca. 1:4 ratio). The major signal was centered at 1.93 ppm flanked by ^{195}Pt satellites with $^1J_{\text{Pt-P}}$ coupling constant of 1848 Hz. In principle, the magnitude of the coupling constant implies the formation of a *trans* isomer [15]. The minor resonance was observed at 38.11 ppm. At this moment, we are unable to properly assign this signal, however, we can speculate that the lowfield shift may originate from the formation of bimetallic species as was described by us previously (Scheme 1) [10,11]. Unfortunately, our attempts to isolate these substances separately failed and we were only able to obtain the major product in an analytically pure form and 48% yield. Interestingly, the employment of the *trans*-PtCl₂(CH₃CN)₂ precursor in this reaction results in the formation of identical products, albeit, in different ratio. ^1H NMR spectrum of **4** exhibited a quite similar pattern to that of **3** except for the chemical shifts of isopropyl methine protons that appeared at δ 2.87 and 4.14 ppm (!), respectively (Fig. 2). This intriguing lowfield shift may result from either steric (van der Waals) repulsion [16] or weak hydrogen bonding [17]. More solid indication, however, might come from the structure elucidation.

2.2. Crystal structure and comparative analysis of the d^8 transition metal complexes

Single crystals of **2**, **3** and **4** were grown by the slow evaporation of their saturated acetonitrile, THF and chlo-

roform solutions, respectively. Having all the new compounds in hands, their exact structural features and coordination preferences have been studied by means of X-ray analysis.

The X-ray structure elucidation of **2** and **3** confirmed the *trans*-spanning chelation modes in both, however, with different structural features (Fig. 3). The nickel center in **2** was heavily distorted from a square planar geometry (Fig. 3 (left)). For example, the observed P(1)–Ni–P(2) and Cl(1)–Ni–Cl(2) angles were 152.51(5)° and 162.60(2)°, respectively. This structure was quite consistent with the observed paramagnetic behavior of **2** in solution. The rhodium center in **3** (Fig. 3 (right)), in opposite, adapts a butterfly-type geometry with P(1)–Rh–P(1') and C(25)–Rh–Cl(1) angles of 149.79° and 170.77°, respectively, that resembles the previously published palladium complexes.

Remarkably, only one of the possible rotamers (roughly, one in which the Cl ligand is in gauche position with respect to the isopropyl groups and the CO ligand points into the space between the triptycene rings) existed in solid state. Looking back at the ^{31}P and ^{13}C NMR characteristics of **3**, only one rotamer existed also in solution. The present rotamer can be, in principle, stabilized by weak interactions between adjacent CO ligand and the corresponding triptycene π -systems as was proposed for other *trans*-spanned L₂Rh(CO)Cl complexes [18].

While the solid-state structures of **2** and **3** were quite predictable based on NMR measurements, the X-ray analysis of **4** was in complete contradiction to the spectroscopic data that predicted a *trans*-coordinated platinum atom (Fig. 4). The geometry around the metal was square planar, albeit strongly distorted due to a large P(1)–Pt–P(2) angle of 109.27°. This distortion consequently leads to the reduced P(1)–Pt–Cl(1), Cl(1)–Pt–Cl(2) and P(2)–Pt–Cl(2) angles that were measured as 83.73°, 81.29° and 84.94°, respectively, as well as to the significantly longer Pt–P bonds that averaged 2.326 Å [19]. Pt–Cl bonds, at the same time, were within the normal range.

Noteworthy, despite our expectations that *cis* coordination of 1,8-bis(diisopropylphosphino)triptycene in transition metal complexes of this type may be attained through the rotation of donors around C–P bonds as was represented in Fig. 1, in actuality, the virtue of an extreme frame deformation allows the formation of a smaller bite and of a shorter nonbonding P...P distance (3.79 Å) in **4**. To contrast: while P...P distances of 4.36–4.45 Å form when the aromatic rings slope at an angle of roughly

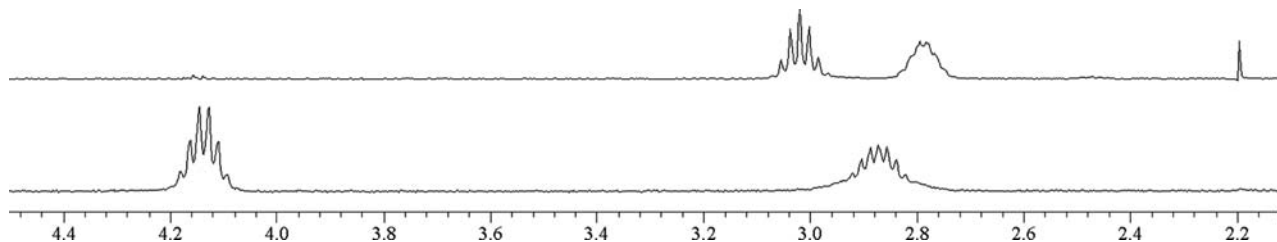


Fig. 2. Extension of the ^1H NMR spectra of **3** (top) vs. **4** (bottom).

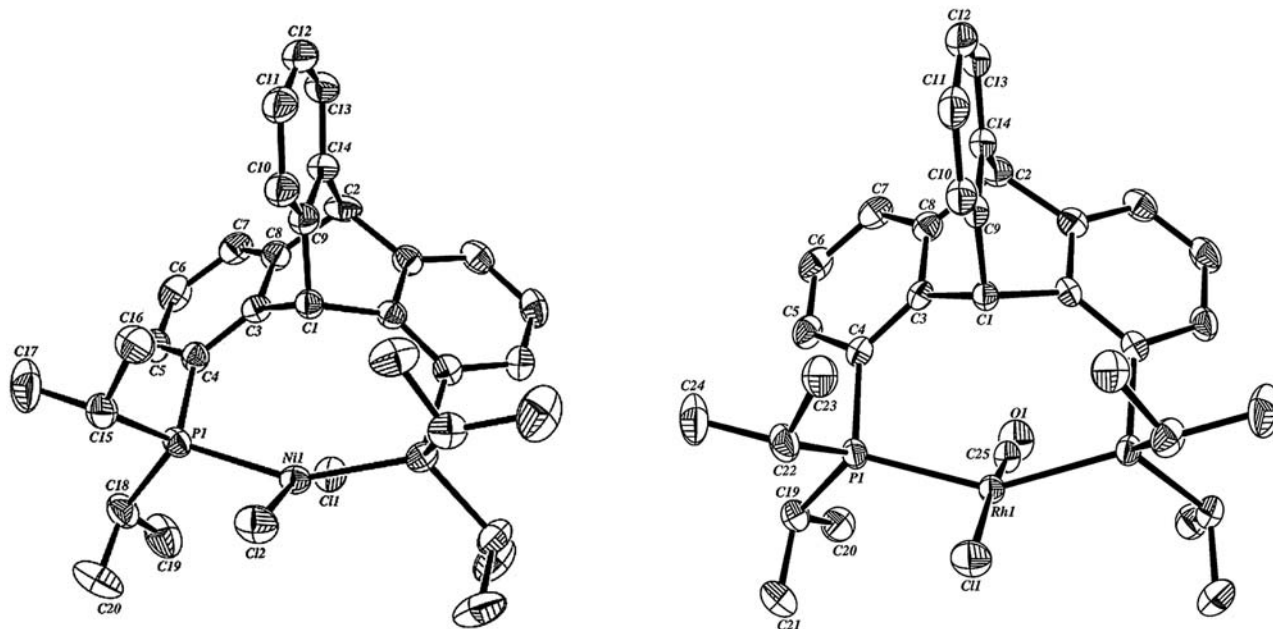


Fig. 3. ORTEP drawings (50% probability ellipsoids) of structures **2** and **3**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) in **2**: Cl(1)–Ni(1) 2.1775(12), Cl(2)–Ni(1) 2.1662(13), Ni(1)–P(1#1) 2.2407(8), Ni(1)–P(1) 2.2407(8), Ni(2)–P(2#2) 2.2476(8), Ni(2)–P(2) 2.2476(8); Cl(2)–Ni(1)–Cl(1) 162.99(5), Cl(2)–Ni(1)–P(1#1) 95.40(3); Cl(1)–Ni(1)–P(1#1) 88.38(3), Cl(2)–Ni(1)–P(1) 95.39(3), Cl(1)–Ni(1)–P(1) 88.38(2), P(1#1)–Ni(1)–P(1) 153.33(5). Selected bond lengths (Å) and angles (°) in **3**: C(25)–O(1) 1.136(6), C(25)–Rh(1) 1.826(5), Cl(1)–Rh(1) 2.3687(12), P(1)–Rh(1) 2.3220(8), Rh(1)–P(1#1) 2.3220(8); C(25)–O(1)–Cl(4) 137.9(4), C(25)–Rh(1)–P(1#1) 87.71(5), P(1)–Rh(1)–P(1#1) 149.79(4), C(25)–Rh(1)–Cl(1) 170.80(16), P(1)–Rh(1)–Cl(1) 94.63(2), P(1#1)–Rh(1)–Cl(1) 94.63(2).

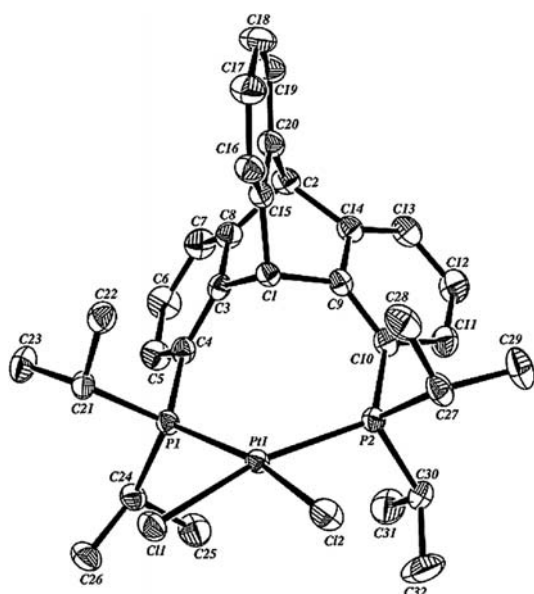


Fig. 4. ORTEP drawing (50% probability ellipsoids) of structure of **4**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) in **4**: Cl(1)–Pt(1) 2.3553(6), Cl(2)–Pt(1) 2.3661(6), P(1)–Pt(1) 2.3208(6), P(2)–Pt(1) 2.3285(6); P(1)–Pt(1)–P(2) 109.27(2), P(1)–Pt(1)–Cl(1) 83.73(2), P(2)–Pt(1)–Cl(1) 166.30(2), P(1)–Pt(1)–Cl(2) 164.64(2), P(2)–Pt(1)–Cl(2) 85.94(2), Cl(1)–Pt(1)–Cl(2) 81.29(2).

120° as was observed in **1–3**, the platinum complex **4** exhibits C(3)···C(8) and C(9)···C(14) interplanar angle of 98.03°. This pathway enabling the variation of the bite

angles was quite unexpected considering the seeming rigidity of the triptycene frame.

On the other hand, the structure depicted in Fig. 4 may also provide a rationalization for unusually shifted isopropyl methine protons observed by ¹H NMR. It is now clear that the significant lowfield shift in **4** (ca. $\Delta\delta = +1.1$ ppm with respect to **1,2** or **3** and $\Delta\delta = +1.75$ ppm with respect to the free ligand) results from C(21)–H···Cl(1)–Pt and C(27)–H···Cl(2)–Pt weak hydrogen bonding interactions. Both C(21)C(22)C(23) and C(27)C(28)C(29) isopropyl groups are locked in such a position that the corresponding methine protons are in close proximity to the chloride atoms: the H···Cl separation averaged ca. 2.55 Å. This distance is significantly lower than the sum of van der Waals radii ($r(\text{H}) = 1.2$ and $r(\text{Cl}) = 1.8$) and the observed C–H–Cl angles are ca. 120°. These parameters meet the criteria of hydrogen bonds and imply the anionic character of the chloride ligands [20].

The existence of these stabilizing interactions may also explain the constrained structure of **4** described previously.

3. Conclusion

The structural analysis of complexes **2–4** revealed that triptycene-based ligands are capable of forming stable chelate compounds with different d⁸ transition metals. It is now clear, that although the ligands favor *trans*-spanning coordination due to remotely located donors, the bent shape of the frame makes for their ability to adapt different



Fig. 5. Superposed models of the triptycene skeleton in **2** (green) vs. **4** (brown). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

bite angles (from 155° in **1** to 109° in **4**), to conform to square planar, butterfly-like or tetrahedron-like geometries, and to form both *cis*- and *trans*-coordinated species. Remarkably, the formation of *cis*-chelated complexes is achieved via deformation of the ligand frame rather than via expected rotation of donors. Although the constrained twist of the skeleton is apparently compensated by weak hydrogen bonding interactions in solid state, the lack of well-pronounced “rotational self-tunability” is somewhat disappointing because crystal and solution behavior are not always identical (see Fig. 5). Therefore, we plan to redesign the ligand so that we could preserve the attractive features of the triptycene scaffold but enhance its flexibility range. This can be achieved by installing more pliable donors (e.g. methylene-bridged) into 1 and 8 positions of triptycene.

4. Experimental

All manipulations were performed using standard Schlenk technique under an atmosphere of dry N_2 . Anhydrous solvents, metal precursors and deuterated solvents were purchased from Aldrich and used without further purification or prepared using published procedures. 1,8-bis(diisopropyl-phosphino)triptycene was prepared following published procedure [10]. NMR spectra were recorded on a Bruker instrument operating at 400 MHz for proton, 100 MHz for carbons and 121 MHz for phosphorus. Diffraction data were collected with a Bruker APEX CCD instrument (Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$)). Crystals were mounted onto glass fibers using epoxy. Single crystal reflection data were collected on a Bruker APEX CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package [21]. The integration of data frames and refinement of cell structure were done by the SAINT+ program package [22] (see Table 1). Refinement of the structure on F^2 was carried out by the SHELXTL software package [23]. Further information may be found within CIF files provided as Supplementary material.

4.1. $[NiCl_2(LI)]$ (**2**)

A solution of **L1** (200 mg, 0.411 mmol) and $NiCl_2(dme)$ (90.3 mg, 0.411 mmol) in acetonitrile (4 mL) was stirred overnight at room temperature. All volatiles were evaporated under reduced pressure. The residue was rinsed with pentane and dried on vacuo, affording **4** as green powder (210 mg, 83%). The deep blue crystals have been obtained by recrystallization from acetonitrile. Anal. Calc. for $C_{32}H_{40}Cl_2P_2Ni$: C, 62.37; H, 6.54. Found: C, 62.32; H, 6.71%.

4.2. $[RhCl(CO)LI]$ (**3**)

A solution of **L1** (400 mg, 0.82 mmol) and $Rh_2Cl_2(CO)_4$ (159.6 mg, 0.41 mmol) in chloroform (8 mL) was stirred at room temperature for 24 h. Analytically pure compound was obtained by slow diffusion of pentane into a saturated chloroform solution (423.6 mg, 79%). Crystals suitable for X-ray analysis were obtained by slow evaporation of the saturated THF solution. 1H NMR (THF- d_8): δ 9.10 (s, 1H), 7.47 (d, 2H, $J = 8$ Hz), 7.41 (d, 1H, $J = 7$ Hz), 7.31 (d, 1H, $J = 7$ Hz), 7.01–7.13 (m, 5H), 6.96 (t, 1H, $J = 8$ Hz), 5.49 (s, 1H), 2.96–3.03 (m, 2H), 2.73–2.85 (m, 2H), 1.54 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 1.44 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 1.16 (dd, 6H, $J = 7$ Hz, $J = 13$ Hz), 1.10 (dd, 6H, $J = 7$ Hz, $J = 8$ Hz). ^{13}C ($CDCl_3$): δ 187.07 (dt, $J_{C-Rh} = 57$ Hz, $J_{C-P} = 15$ Hz), 152.03 (t, $J = 8$ Hz), 147.52, 147.36 (t, $J = 4$ Hz), 144.08, 129.13 (t, $J = 19$ Hz), 127.57, 125.83, 125.70, 125.37, 124.71, 123.77 (t, $J = 3$ Hz), 122.96, 55.23, 54.96 (t, $J = 6$ Hz), 24.21 (t, $J = 10$ Hz), 23.57 (t, $J = 10$ Hz), 20.99, 20.47 (t, $J = 3$ Hz), 18.25 (t, $J = 6$ Hz), 16.05. ^{31}P NMR (THF- d_8): δ 38.16 (d, $J_{P-Rh} = 127$ Hz). Anal. Calc. for $C_{33}H_{40}ClOP_2Rh$: C, 60.70; H, 6.17. Found: C, 60.57; H, 6.01%.

4.3. $[PtCl_2(LI)]$ (**4**)

A solution of **L1** (200 mg, 0.411 mmol) and *cis*- $PtCl_2(CH_3CN)_2$ (143 g, 0.411 mmol) in acetonitrile (4 mL) was stirred overnight at room temperature. All volatiles were evaporated under reduced pressure. The residue was recrystallized from pentane/chloroform mixture **4** as yellowish crystals (147 mg, 48%). 1H NMR ($CDCl_3$): δ 8.95 (s, 1H), 7.65 (d, $J = 7.05$ Hz, 2H), 7.38 (d, $J = 5$ Hz, 2H), 7.30 (t, $J = 8.05$ Hz, 1H), 7.23 (t, $J = 8.05$ Hz, 1H), 6.93–7.01 (m, 4H), 5.48 (s, 1H), 4.09–4.19 (m, 2H), 2.78–2.95 (m, 2H), 1.59 (dd, $J = 10$ Hz, $J = 8$ Hz, 6H), 1.38 (dd, $J = 11$ Hz, $J = 7$ Hz, 6H), 1.23 (dd, $J = 11$ Hz, $J = 7$ Hz, 6H), 0.63 (dd, $J = 7$ Hz, $J = 7$ Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 150.31 (t, $J = 4.07$ Hz), 147.96 (t, $J = 3.07$ Hz), 142.4, 138.79, 127.51, 126.77, 126.17, 125.92 (t, $J = 4.07$ Hz), 123.92 (t, $J = 3.3$ Hz), 123.82, 117.64, 117.22, 54.69, 46.86 (t, $J = 10$ Hz), 26.27 (d, $J = 36.6$ Hz), 24.66 (d, $J = 33.3$ Hz), 21.46, 20.13, 20.05, 16.94. ^{31}P NMR ($CDCl_3$): δ 1.93 (t, $J = 1844$ Hz). Anal. Calc. for

Table 1
Crystal data and structure refinement details for **2**, **3** and **4**

Compound	2	3	4
Empirical formula	C _{34.63} H _{43.88} Cl ₂ N _{1.50} NiP ₂	C ₃₅ H ₄₂ Cl ₇ OP ₂ Rh	C ₃₄ H ₄₂ Cl ₈ P ₂ Pt
Formula weight	672.64	891.69	991.31
<i>T</i> (K)	295(1)	173(1)	173(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>Pbca</i>
Unit cell dimensions			
<i>a</i> (Å)	14.1867(8)	21.0458(18)	18.7108(12)
<i>b</i> (Å)	16.0066(9)	14.4555(12)	18.6227(12)
<i>c</i> (Å)	30.4255(16)	12.7421(11)	22.1204(14)
α (°)	90°	90°	90°
β (°)	90°	90°	90°
γ (°)	90°	90°	90°
<i>V</i> (Å ³)	6909.0(7)	3876.5(6)	7707.8(9)
<i>Z</i>	8	4	8
<i>D</i> _{calc} (Mg/m ³)	1.293	1.528	1.709
Absorption coefficient (mm ⁻¹)	0.834	1.034	4.303
<i>F</i> (000)	2833	1816	3920
Crystal size (mm)	0.32 × 0.23 × 0.16	0.27 × 0.24 × 0.20	0.34 × 0.26 × 0.25
θ Range for data collections (°)	1.92–27.00	1.87–28.02	1.80–27.00
Limiting indices	−18 ≤ <i>h</i> ≤ 18, 20 ≤ <i>k</i> ≤ 20, −38 ≤ <i>l</i> ≤ 38	−27 ≤ <i>h</i> ≤ 27, 19 ≤ <i>k</i> ≤ 19, −16 ≤ <i>l</i> ≤ 16	−23 < <i>h</i> < 23, −23 < <i>k</i> < 23, −28 < <i>l</i> < 28
Number of reflections collected	38927	44371	34337
Number of independent reflections (<i>R</i> _{int})	7836 (0.0363)	4843 (0.0338)	8400 (0.0532)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Number of data/restraints/parameters	7836/1/405	4843/6/245	8400/0/414
Goodness-of-fit on <i>F</i> ²	0.992	1.108	1.086
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0392, <i>wR</i> ₂ = 0.0985	<i>R</i> ₁ = 0.0498, <i>wR</i> ₂ = 0.1396	<i>R</i> ₁ = 0.0222, <i>wR</i> ₂ = 0.0584
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.1008	<i>R</i> ₁ = 0.0536, <i>wR</i> ₂ = 0.1423	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0591

C₃₂H₄₀Cl₂P₂Pt: C, 51.07; H, 5.36. Found: C, 50.77; H, 5.47%.

Acknowledgements

This research was supported by The Israel Science Foundation (Grant No. 866/06). We also thank Dr. Shmuel Cohen for solving X-ray structures.

Appendix A. Supplementary material

X-ray crystallographic files in CIF format for all structures. Copies of ¹H, ¹³C and ³¹P NMR spectra of all mentioned compounds. CCDC 613525, 617158 and 613524 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.09.065](https://doi.org/10.1016/j.jorganchem.2006.09.065).

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