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Communications

Nine-Membered Trans Square-Planar Chelates Formed by a bisbi Analogue

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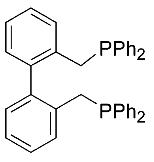
Summary: The new diphosphine o-$C_6H_4\{CH_2P(C_8H_{14})\}_2$*, containing the "bisbi" backbone, forms mononuclear trans chelates with rhodium(I), nickel(II), palladium(II), and platinum(II), as shown by X-ray crystallography, NMR spectroscopy, and mass spectrometry.*

Rhodium complexes of 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (bisbi) are exceptionally active and selective hydroformylation catalysts.[1] Casey calculated that bisbi could span angles from 92 to 155° and remain within the 3 kcal mol^{-1} strain potential energy well, thought to define accessible ligand geometries.[2] Crystal structures have borne out this prediction,[1−6] with bite angles in known bisbi complexes being in the range 103.5−152.0°.



bisbi

It has been proposed that the high catalytic activity of rhodium−bisbi complexes arises because the flexibility of the bisbi backbone allows low-strain access to the 90 and 120° bite angles present in the various intermediates in the hydroformylation catalytic cycle.[7]

Here we report that the bisbi analogue **1** forms square-planar complexes (surprisingly, there are no previous reports of square-planar complexes of bisbi) and, unexpectedly, that **1** can span trans sites in a nine-membered chelate ring. van Leeuwen et al.[8] predicted that ligands that can span trans positions may show high activity in hydroformylation. The topic of trans-spanning ligands is of considerable current interest[9,10] and has been reviewed recently.[11]

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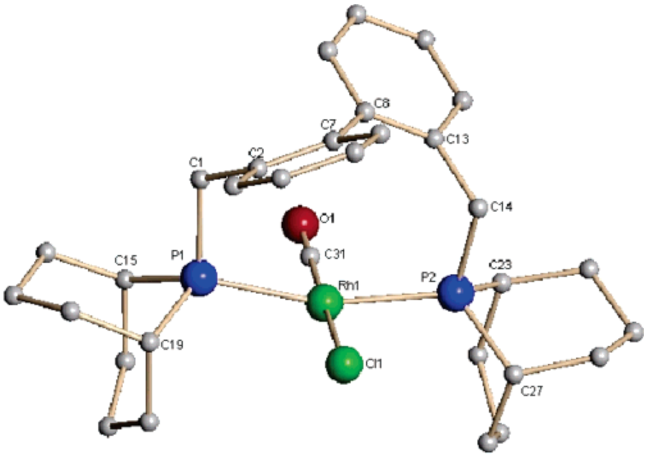
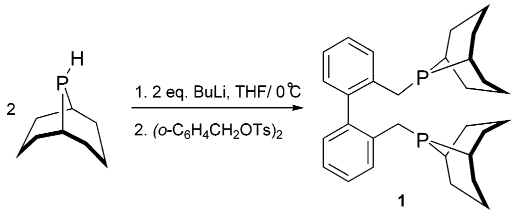


Figure 1. Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (deg): Rh(1)−C(31), 1.803(7); Rh(1)−Cl(1), 2.3904(14); O(1)−C(31), 1.146(10); Rh(1)−P(1), 2.2994(8); Rh(1)−P(2), 2.3024(8); P(1)−Rh(1)−P(2), 162.07(3); C(31)−Rh(1)-Cl(1), 179.47(16).

Ligand **1** was synthesized from pure 9-phosphabicyclo[3.3.1]nonane[12] in 90% yield and has been fully characterized (eq 1).



(1)

Dropwise addition of **1** to $[RhCl(CO)_2]_2$ in CH_2Cl_2 gave the trans chelate complex **2** in quantitative yield, as shown by a combination of elemental analysis, FAB mass spectrometry, IR spectroscopy (ν_{CO} 1957 cm^{-1}), and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum was particularly informative: two signals at δ 22.1 and 15.4 with coupling to ^{103}Rh ($^1J(RhP)$ for both being 122 Hz) and a large $^2J(PP)$ value of 350 Hz, showing that the two P atoms are inequivalent and trans to each other.

The reason for the inequivalence of the P atoms is evident from the crystal structure (see Figure 1). While the ligand conformation is approximately C_2 symmetric, the asymmetry of the Rh(I) coordination environment (due to the Cl and CO ligands) renders the phosphorus atoms inequivalent. Crystals of **2**, as its dichloromethane solvate, show the distorted-square-planar coordination geometry at rhodium with a *trans*-P−Rh−P angle of 162.07(3)°.

Treatment of $[PdCl_2(NCPh)_2]$ with **1** gave the trans chelate complex **3**. The crystal structure of **3**, as its dichloromethane solvate, is essentially isostructural with that of **2** (Figure 2), except that the complex has higher symmetry (approximately C_2). The Pd(II) coordination geometry is distorted-square-planar, and the *trans*-P−Pd−P angle is 163.59(4)°.

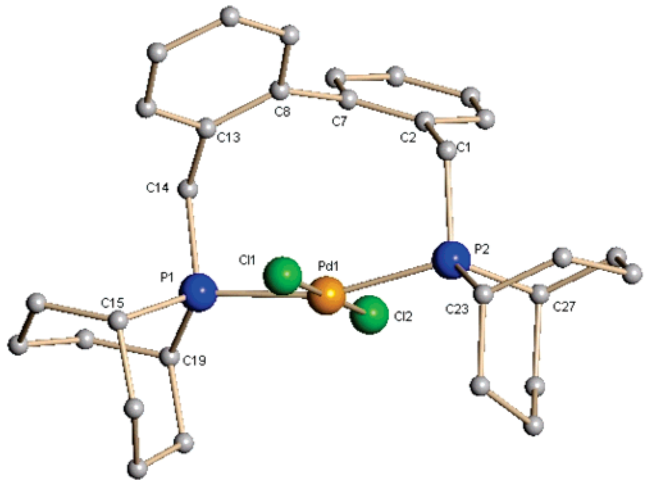


Figure 2. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (deg): Pd(1)−P(1), 2.2987(12); Pd(1)−P(2), 2.3040(13); Pd(1)−Cl(2), 2.3165(14); Pd(1)−Cl(1), 2.3184(14); P(1)−Pd(1)−P(2), 163.59(4); Cl(2)−Pd(1)−Cl(1), 179.61(5).

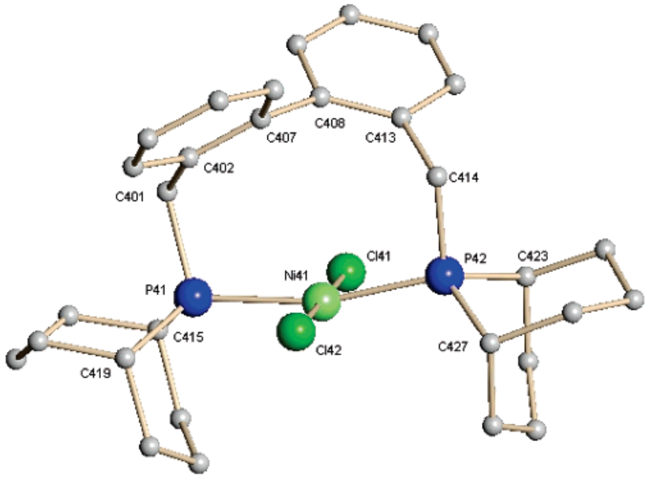


Figure 3. Molecular structure of one of the four independent molecules in **4**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (deg): Ni(41)−P(41), 2.210(2); Ni(41)−P(42), 2.209(2); Ni(41)−Cl(41), 2.175(2); Ni(41)−Cl(42), 2.169(2); P(42)−Ni(41)−P(41), 165.48(9); Cl(42)−Ni(41)−Cl(41), 179.38(10).

The reaction of **1** with $NiCl_2{\cdot}6H_2O$ in C_2H_5OH/CH_2Cl_2 furnishes the orange complex **4** in 85% yield and was fully characterized. A singlet at δ −1.4 is observed in the $^{31}P\{^1H\}$ NMR spectrum, and the $^{13}C\{^1H\}$ NMR spectrum shows six sharp signals for the aromatic carbons, confirming the C_2 symmetry of the complex. Complex **4** crystallizes as an ether solvate in the space group $P\bar{1}$ with four molecules of the complex and one ether per asymmetric unit (Figure 3). The structure is distorted-square-planar. The trans-spanning angle, as determined from the four independent values in the crystal structure, is in the range 163.7(1)−165.5(1)°.

An attempt to make the platinum analogue of **3** by addition of **1** to $[PtCl_2(cod)]$ gave instead the cis chelate **6** in 85% yield, which was fully characterized. The

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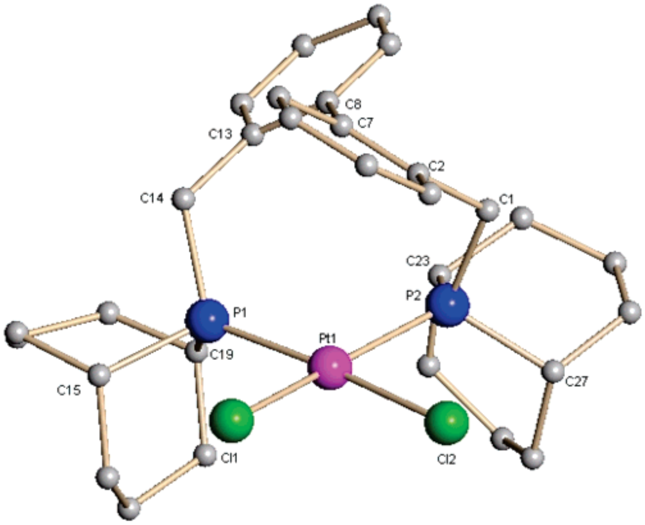

Figure 4. Molecular structure of **6**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (deg): Pt(1)−P(1), 2.2798(9); Pt(1)−P(2), 2.2627(9); Pt(1)−Cl(1), 2.3566(9); Pt(1)−Cl(2), 2.3632(9); P(1)−Pt(1)−P(2), 101.76(3); Cl(2)−Pt(1)−Cl(1), 84.26(3).

$^{31}P\{^1H\}$ NMR spectrum of **6** in CH_2Cl_2 revealed two sharp signals at δ 1.6 and −3.5 with values of $^1J(PtP)$ (3549 and 3746 Hz) and $^2J(PP)$ (16 Hz) which are consistent with a cis geometry with inequivalent P atoms. The bite angle of **1** in complex **6**, as determined from the crystal structure (Figure 4), is 101.76(3)°.

The inequivalence of the P atoms detected in the solution NMR of **6** can be explained if the ring conformation present in the solid state is also adopted in solution. No broadening of the $^{31}P\{^1H\}$ signals takes place when samples are heated to 130 °C in $C_2H_2Cl_4$, which indicates that the ring is remarkably conformationally rigid in this unusual chiral chelate. Thus, ligand **1** is an example of a *tropos* ligand: i.e. one whose axial chirality can only be resolved on coordination to a metal.[13]

Addition of **1** to $K[PtCl_3(C_2H_4)]$ gave the trans isomer **5** quantitatively, as shown by elemental analysis, mass spectrometry, and particularly $^{31}P\{^1H\}$ NMR spectroscopy, which showed a singlet at δ 9.9 with a $^1J(PtP)$ value of 2500 Hz, consistent with trans chelation. Solutions of complex **5** were heated to 130 °C in $C_2H_2Cl_4$, and after 2 days, the $^{31}P\{^1H\}$ NMR spectrum of the solution showed the presence of the cis isomer **6** (30%). Thus, at elevated temperatures *trans*-**5** slowly isomerizes to *cis*-**6**. Note that, under similar conditions, no isomerization of *cis*-**6** to *trans*-**5** was observed, which suggests that the cis isomer is thermodynamically more stable, at least for $[PtCl_2(\mathbf{1})]$ in $C_2H_2Cl_4$ solution.[14]

These results have established that **1**, which contains the same backbone as bisbi, can readily span trans positions in square-planar complexes of Rh, Pd, and Pt. Recent results have shown that palladium complexes of **1** catalyze the formation of monobutenyl ethers from butadiene and alcohols in good yields.[15]

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Supporting Information Available: Text giving preparative procedures and spectroscopic and elemental analysis data for compounds **1**−**6** and CIF files giving crystallographic data sets for **2**−**4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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