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Unexpected Formation of Ruthenium(II) Hydrides from a Reactive Dianiline Precursor and 1,2-$(Ph_2P)_2$-1,2-*closo*-$C_2B_{10}H_{10}$

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Reaction of the new precursor *cis,trans*-Ru(cod)$(anln)_2Cl_2$ with the diphosphine 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane (*o*-dppc) unexpectedly results in two new ruthenium(II) hydrides, *trans*-Ru$(o\text{-dppc})_2$(H)Cl and the neutral, five-coordinate complex Ru(*o*-dppc)(*nido*-dppc)(H), depending upon the reaction conditions [anln is aniline and *nido*-dppc is 7,8-$(Ph_2P)_2C_2B_9H_{10}{}^-$]. Chloride abstraction from *trans*-Ru$(o\text{-dppc})_2$(H)Cl leads to another five-coordinate hydride, $[Ru(o\text{-dppc})_2(H)]^+$, which is isolated as either a triflate or hexafluorophosphate salt. On the basis of labeling and reactivity studies, the source of the hydride appears to be the cod ligand.

During the course of our search for new precursors for the preparation of oligometallic molecular assemblies, we have discovered an extremely reactive ruthenium(II) dianiline complex, *cis*,*trans*-Ru(cod)$(anln)_2Cl_2$ (**1**; anln is aniline), which by virtue of its stereochemistry and the nature of the ligands can exhibit selective, stepwise substitutions at pairs of cis-coordination sites. In complex **1**, the labile anln ligands are capable of being substituted under mild conditions because of the hard—soft nature of their interaction, the chloride ligands can undergo ligand metathesis via salt formation, and the strongly bound cod ligand can be replaced by selective photochemical substitution. Potential applications of this and related complexes range from the preparation of isomerically pure octahedral molecular squares, and linear oligomeric complexes,[1] to new bis-chelate complexes of the type *trans*-Ru(chelate)$_2Cl_2$ or *trans*-Ru(chelate)(chelate′)Cl_2. Apparently, ruthenium(II) aniline complexes are scarce despite their obvious appeal as precursors containing good leaving groups.[2]

In this Communication, we present details of the reaction of complex **1** with the chelate 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane [1,2-$(Ph_2P)_2$-1,2-*closo*-$C_2B_{10}H_{10}$; *o*-dppc], which surprisingly results in the formation of the hydride complex *trans*-Ru$(o\text{-dppc})_2$(H)Cl (**2**). Complex **2** is also a precursor for the formation of new 16-electron, five-coordinate hydrides by both adventitious and designed means. Collectively, these reactions constitute new routes to ruthenium(II) hydride complexes.[3] In addition, the complexes described here are the first examples containing two *o*-dppc ligands at one metal center.

The preparation of complex **1** is modeled on that of the ditoluidine complex, which, in our hands, is highly insoluble in common organic solvents, limiting its viability as a reactive precursor.[4] Complex **1** is easily and inexpensively prepared in high yields (ca. 95%) from the cod polymer di-μ-chloro-$[RuCl_2(\eta^4\text{-}C_8H_{12})]_x$ ($x > 2$).[5] It should be noted that a similar starting material, *cis*,*trans*-Ru(cod)$(CH_3CN)_2Cl_2$, is prepared[6,7] in an analogous fashion, which when reacted with *o*-dppc gives different products (see later). Crystal structure data for complex **1** are given along with selected bond lengths and angles in Figure 1. The structure shows a distorted octahedral environment with a drastically bent Cl−Ru−Cl angle at 156.54(4)°, a common distortion found for ligands axial to the equatorial plane containing cod in ruthenium(II) complexes.[7,8]

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[5] ***cis,trans*-Ru. (cod)(anln)$_2$Cl$_2$ (1).** The polymer di-μ-chloro-$[RuCl_2(\eta^4\text{-}C_8H_{12})]_x$ ($x > 2$; 5.00 g, ~17.8 mmol) and anln (12 mL, 126.1 mmol) were placed in a 100-mL round-bottomed flask equipped with a magnet. The reaction was placed in an oil bath at 90 °C with stirring for 1 h. The reaction was cooled to room temperature, and the product was precipitated with diethyl ether. The product was then redissolved in chloroform (150 mL) and filtered by suction filtration to remove a small amount of insoluble material. The volume of the filtrate was reduced by rotary evaporation to 15 mL, a microcrystalline cream-colored precipitate formed during the volume reduction, and the product was further precipitated by adding diethyl ether. The cream-colored product was collected by suction filtration, washed several times with diethyl ether, and dried under vacuum (6.99 g, 94% yield). Suitable crystals for single-crystal X-ray diffraction were grown by slow evaporation of the aniline diethyl ether filtrate, which was placed in a freezer at –10 °C. Anal. Calcd: C, 51.62; H, 5.62; N, 6.01. Found: C, 51.50; H, 5.61; N, 5.99. ^{1}H NMR (chloroform-*d*): δ 7.332 (d, 4H), 7.259 (t, 4H), 7.128 (t, 2H), 4.560 (s, 4H), 3.705 (s, 4H), 2.563 (m, 4H), 1.955 (d, 4H).

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10.1021/ic701871t CCC: $40.75

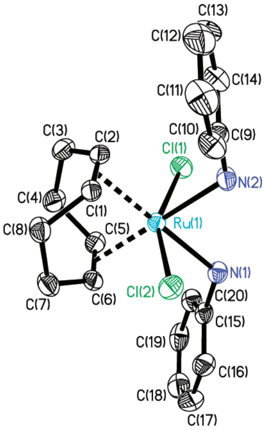

Figure 1. ORTEP representation of **1**. Hydrogen atoms and an anln of crystallization are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) are as follows: Ru(1)−C(1), 2.189(3); Ru(1)−C(2), 2.193(4); Ru(1)−C(6), 2.193(4); Ru(1)−C(5), 2.198(4); Ru(1)−N(1), 2.201(3); Ru(1)−N(2), 2.209(3); Ru(1)−Cl(2), 2.4250(11); Ru(1)−Cl(1), 2.4343(12). Selected bond angles (deg) are as follows: N(1)−Ru(1)−N(2), 84.98(11); Cl(2)−Ru(1)−Cl(1), 156.54(4).

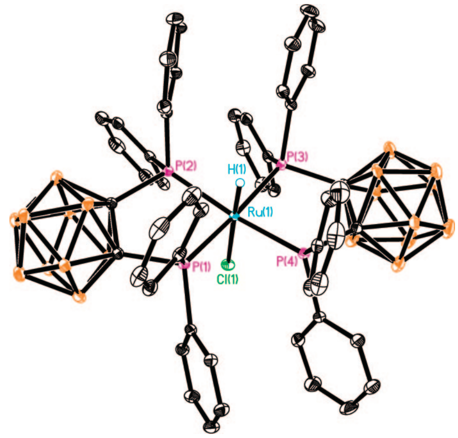

Figure 2. ORTEP representation of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except those of the hydride ligand are omitted for clarity. Selected bond lengths (Å) are as follows: Ru(1)−P(2), 2.3410(4); Ru(1)−P(1), 2.3444(4); Ru(1)−P(3), 2.3465(4); Ru(1)−P(4), 2.3560(4); Ru(1)−Cl(1), 2.5142(4); Ru(1)−H(1), 1.51(2). Selected bond angles (deg) are as follows: P(2)−Ru(1)−P(1), 86.842(15); P(3)−Ru(1)−P(4), 88.515(15); Cl(1)−Ru(1)−H(1), 177.3(8).

Initial studies of the reactivity of complex **1** with chelating diphosphines (PP), for example, 1,2-bis(diphenylphospino)-methane and *cis*-1,2-bis(diphenylphospino)ethylene, showed that within minutes in dichloromethane at room temperature *trans*-Ru(PP)$_2$Cl$_2$ complexes are formed quantitatively. The attempt to expand this reactivity to the *o*-dppc ligand resulted in no reaction under the same conditions; however, when heated to reflux in chlorobenzene or xylene, a yellow microcrystalline precipitate is formed. This complex was not the expected *trans*-dichloride but rather the hydride complex **2**, which subsequently was structurally characterized (Figure 2; along with selected bond lengths and angles).

Complex **2** can be used further to make two 16-electron, five-coordinate complexes. When the reaction is carried out to make complex **2** under more forcing conditions such as longer reflux times (12 h, xylenes) or the reaction is simply refluxed in the higher-boiling solvent *o*-dichlorobenzene for 3 h, complex **1** is converted into the neutral five-coordinate complex Ru(*o*-dppc)(*nido*-dppc)(H) (**3**), where *nido*-dppc is a monoanionic, partially degraded form of *o*-dppc that results from the removal of a single BH vertex and protonation of the open face, resulting in a *nido*-7,8-(Ph$_2$P)$_2$C$_2$B$_9$H$_{10}^-$ ligand.[10]

^{31}P NMR studies convincingly show that slow conversion of complex **2** to **3** occurs under the more forcing conditions. The formation of *nido*-7,8-(Ph$_2$P)$_2$C$_2$B$_9$H$_{10}^-$ from *o*-dppc in the presence of a Lewis base has been demonstrated by Teixidor et al. and is enhanced by metal coordination.[11,12] It is likely that the free anln produced upon substitution is a contributing factor to cage degradation. Complex **3** showed a loss of phosphorus equivalency, indicated by the two ^{31}P{^{1}H} NMR signals at 98.1 and 60.2 ppm that were split with a *trans*-phosphine coupling constant of 208 Hz. The hydride was spectroscopically characterized by ^{1}H NMR spectroscopy as a seven-line multiplet at –30.2 ppm arising from the fortuitous overlap of a triplet of triplets due to one of the dppc-type ligands having a J_{PH} value that is double the other and exhibiting coupling constants of 24 and 12

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(9) ***trans*-Ru(*o*-dppc)$_2$(H)Cl (2).** Complex **1** (0.200 g, 0.429 mmol) and *o*-dppc (0.441 g, 0.861 mmol) were added to a 50-mL round-bottomed flask. This flask was evacuated, and about 7 mL of dry *o*-xylene was added via vacuum transfer. The reaction was refluxed with magnetic stirring for 3 h under a N$_2$ atmosphere. The brown suspension turned to a yellow precipitate. The suspension was then cooled to room temperature, and the yellow product was collected via suction filtration (0.228 g, 46% yield). Suitable crystals for single-crystal X-ray diffraction were grown by slow evaporation of a saturated solution in chloroform. Anal. Calcd for {Ru(*o*-dppc)$_2$(H)Cl·C$_8$H$_{10}$}: C, 56.58; H, 5.62. Found: C, 56.62; H, 5.56.^{1}H NMR (chloroform-*d*): δ 7.705 (s, 8H, broad), 7.631 (d, 8H, broad), 7.259 (t, 4H), 7.197 (t, 4H), 6.960 (m, 16H), –17.372 (qnt, 1H, hydride, J_{PH} = 21 Hz).^{31}P{^{1}H} NMR (chloroform-*d*): δ 89.6 (s).^{11}B NMR (acetone-*d*$_6$): δ –1.01 (s, 6B, broad), –7.78 (s, 4B, broad). The complex was also made by adding 0.150 g (0.126 mmol) of Ru(PPh$_3$)$_3$(H)Cl with 0.167 g (0.325 mmol) of dppc to a 25-mL flask containing 7 mL of *o*-xylene. The reaction was refluxed with stirring for 3 h, which precipitated the yellow product. The product was collected via suction filtration and rinsed with diethyl ether (0.130 g, 88% yield).^{1}H and^{31}P{^{1}H} NMR spectra were in agreement with the preceding values. Note: this complex incorporates solvents depending on conditions and subsequent recrystallizations, which are observed in^{1}H NMR spectra.

(10) **Ru(*o*-dppc)(*nido*-dppc)(H) (3).** Complex **1** (0.200 g, 0.429 mmol) and *o*-dppc (0.441 g, 0.861 mmol) were added to a 50-mL round-bottomed flask containing about 6 mL of *o*-dichlorobenzene. The reaction was refluxed with magnetic stirring for 3 h. The brown suspension turned to a dark-colored solution. The solution was then cooled to room temperature. Upon cooling, the product precipitated as a yellow microcrystalline solid. The crude product was collected via suction filtration and was subsequently purified by dissolving it in a large volume of methylene chloride and then reducing the volume via rotary evaporation, allowing the flask to cool upon solvent evacuation. Upon reduction of the volume, the pure product precipitated out as a yellow microcrystalline solid, which was collected via suction filtration (0.245 g, 51% yield). Anal. Calcd: C, 55.99; H, 5.42. Found: C, 56.24; H, 5.60.^{1}H NMR (chloroform-*d*): δ 8.083 (t, 5H), 7.837 (t, 3H) 7.745 (t, 5H), 7.079 (m, 13H), 6.803 (t, 6H), 6.519 (m, 8H), –2.349 (broad, 1H, BHB), –30.211 (tt, 1H, hydride, $J_{PH}{}^1$ = 24 Hz, $J_{PH}{}^2$ = 12 Hz).^{31}P{^{1}H} NMR (chloroform-*d*): δ 98.1 (d, $J_{PP-trans}$ = 207 Hz), 60.2 (d, $J_{PP-trans}$ = 209 Hz).^{11}B NMR (chloroform-*d*): δ –1.99 (s, 2B, broad), –7.71 (s, 3B, broad), –12.42 (s, 4B, broad), –15.49 (m, 8B, broad), –27.32 (s, 1B, broad), –34.90 (s, 1B, broad). Complex **3** is stable in air as a solid and in solution for about 2 days; after that, the complex undergoes decomposition to form an uncharacterized white species.

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Hz. The BHB bridging proton was located as a broad signal at –2.3 ppm.[12] There was no evidence in the ^{1}H NMR spectrum for an agositic B−H−Ru interaction in solution involving the *nido*-dppc ligand; however, this does not preclude its existence in the solid state.[13] The ^{11}B NMR signals also reflected the loss in symmetry of the carborane cages. The typical *o*-dppc 4:6 splitting pattern is overlaid with the typical *nido*-dppc 2:3:2:1:1 splitting in the range from –2 to –35 ppm. This neutral, coordinatively unsaturated complex is the first to contain both an *o*-dppc ligand and a *nido*-dppc ligand and may have application as an active catalyst for Kharasch additions.[14,15]

A second five-coordinate hydride was prepared in a fashion similar to approaches taken by others,[16–18] using chloride abstraction with either AgOTf or $TlPF_6$ to generate the monocationic five-coordinate complex *trans*-$[Ru(o\text{-}dppc)_2(H)]^+$ in high yield (>90%).[19] Structural data for $[Ru(o\text{-}dppc)_2(H)][PF_6]$ (**4**) are displayed in Figure 3 along with selected bond lengths and angles. Unlike the case of complex **2**, the hydride ligand could not be located. Here, the halves of crystallographically unique cations are present in the asymmetric unit, with the metal centers being located on 2-fold symmetry axes, although they share nearly identical structural features. The four ligating phosphorus atoms and the central ruthenium atom are coplanar, indicating possible disorder of the hydride ligand above and below the RuP_4 plane. Perhaps as a consequence of this, the hydride could not be located in the Fourier maps. The five-coordinate cationic species is air-stable for several days in CH_2Cl_2 and is apparently more robust than similar complexes with other diphosphine ligands.[20] Sixteen-electron metal hydride complexes have traditionally been used for hydrogenation of alkynes and asymmetric transfer hydrogenation.[20,21] Other five-coordinate ruthenium(II) hydrides are useful for the coordination of small molecules (most notably dihydrogen) and also have been found to initiate C−F bond activation of perfluoroalkanes.[22]

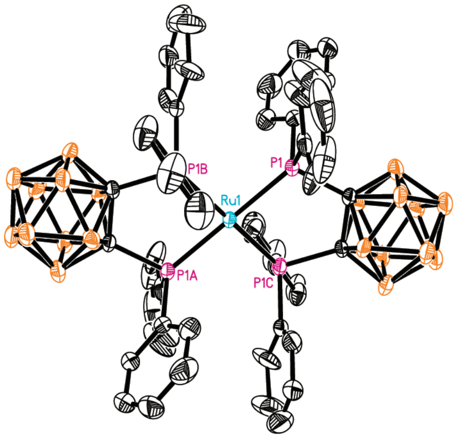

Figure 3. ORTEP representation of the cation in *trans*-**4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are as follows: Ru1−P1, 2.3515(7); Ru1−P1A, 2.3515(7); Ru1−P1C, 2.3423(7); Ru1−P1B, 2.3423(7). Selected bond angles (deg) are as follows: P1C−Ru1−P1B, 180; P1C−Ru1−P1B, 92.28; P1B−Ru1−P1A, 87.72; P1C−Ru1−P1, 87.72; P1C−Ru1−P1A, 92.26; P1−Ru1−P1A, 180.

A series of studies implicate the cod ligand as the source of the hydride. First, a labeling study using *cis*,*trans*-$Ru(cod)(anln\text{-}d_7)_2Cl_2$ showed the formation of the hydride **2** but no incorporation of deuterium. Second, the reaction of *o*-dppc with a non-cod-containing ruthenium(II) source, $Ru(PPh_3)_3Cl_2$, resulted in an insoluble orange precipitate but no hydride complexes. Third, intentional addition of a small amount of water or D_2O to the reaction in xylene did not change the course of the reaction or its yield. Fourth, the reaction of dppc with *cis*,*trans*-$Ru(cod)(CH_3CN)_2Cl_2$ gave a 10% yield of complex **2**, with the remaining ruthenium appearing as a pale-orange insoluble complex. Last, an analysis of the filtrate from complex **1** synthesis using ^{31}P and ^{1}H NMR spectroscopy revealed only unreacted and coordinated *o*-dppc ligands, thereby arguing against ligand degradation as a substantial source of the hydride. Given the unusual nature of this chemistry, we are exploring the reaction of complex **1** with other electron-poor phosphines.

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(19) ***trans*-$[Ru(o\text{-}dppc)_2(H)][OTf]$.** Complex **2** (0.200 g, 0.172 mmol) and AgOTf (0.049 g, 0.191 mmol) were added to a 50-mL round-bottomed flask containing about 25 mL of 1,2-dichloroethane. The reaction was covered with aluminum foil and refluxed with magnetic stirring for 3 h. The yellow suspension turned to a red solution. The solution was then cooled to room temperature, the AgCl was filtered from the supernatant, and the solvent was removed by rotary evaporation. A minimum amount of methylene chloride was added to dissolve the product, and diethyl ether was added to precipitate an orange solid, which was collected via suction filtration and dried under vacuum (0.206 g, 94% yield). Suitable crystals for single-crystal X-ray diffraction were grown by slow evaporation of a saturated solution in methylene chloride. Anal. Calcd: C, 49.88; H, 4.82. Found: C, 50.00; H, 4.90.^{1}H NMR (acetone-d_6): δ 7.896 (s, 8H, broad), 7.543 (m, 8H), 7.405 (m, 16H), 7.049 (s, 8H, broad), –27.031 (qnt, 1H, hydride, J_{PH} = 19 Hz).$^{31}P\{^{1}H\}$ NMR (acetone-d_6): δ 88.0 (s).^{11}B NMR (acetone-d_6): δ –1.01 (s, 6B, broad), –7.78 (s, 4B, broad). ESI-MS. Calcd: *m/z* 1127.5. Found: *m/z* 1127.7. ***trans*-$[Ru(o\text{-}dppc)_2(H)][PF_6]$ (4).** This complex was prepared and purified in the same manner as that of *trans*-$[Ru.\ (dppc)_2(H)][OTf]$ using 0.066 g (0.189 mmol) of $TlPF_6$ instead of AgOTf (0.198 g, 91% yield). Anal. Calcd: C, 49.09; H, 4.83. Found: C, 48.83; H, 4.82.^{1}H NMR (acetone-d_6): δ 7.892 (s, 8H, broad), 7.545 (m, 8H), 7.401 (m, 16H), 7.033 (s, 8H, broad), –26.969 (qnt, 1H, hydride, J_{PH} = 19 Hz).$^{31}P\{^{1}H\}$ NMR (acetone-d_6): δ 88.0 (s).

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