Organometallic Supramolecular Mixed-Valence Cobalt(I)/Cobalt(II) Aquo Complexes Stabilized with the Water-Soluble Phosphine Ligand *p*-TPPTP (*p*-triphenylphosphine triphosphonic acid)

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Reaction of the water-soluble phosphine phosphonic acid *p*-TPPTP(H)$_6$ (*p*-triphenylphosphine triphosphonic acid) with $Co_2(CO)_8$ under biphasic conditions results in the formation of $Co_6(CO)_3$(*p*-TPPTP)$_2$$(H_2O)_{24}$•$24H_2O$ (**2**) or $Co_4(CO)_3$(*p*-TPPTP)$_2$$(H_2O)_{24}$•$24H_2O$ (**3**) depending on the pH of the solution. These supramolecular organometallic Co(I)/Co(II) complexes contain either six (**2**) or four (**3**) crystallographically distinct cobalt ions. The cation [Co(CO)$_3$(*p*-TPPTP)$_2$]$^+$ from **2** was reacted with titanium tetraisopropoxide via a sol−gel method to give a titania-supported Co(I) olefin hydroformylation catalyst, which was characterized using solid-state ^{31}P NMR, IR, and XPS.

Introduction

Mixed-valence Co(I)/Co(III) coordination complexes are currently of interest due to their potential use as single molecular magnets, the "smallest conceivable memory devices".[1] Mixed-valence Co(I)/*Co(II)* are much rarer, and their study is relevant to the redox chemistry of vitamin B$_{12}$.[2] Vitamin B$_{12}$ is a rare example of a naturally occurring organometallic complex, but despite this fact, to the best of our knowledge no structural characterizations of mixed-valence *organometallic* Co(I)/Co(II) complexes have been reported. We have been studying the coordination chemistry of the simple phosphonic acid−phosphine ligand triphenylphosphine triphosphonic acid,[3] *p*-TPPTP(H)$_6$, with a variety of transition metals and the subsequent use of the resulting complexes in aqueous phase and supported catalysis.[4] This phosphine can be considered a hard−soft donor ligand that has the potential to stabilize different oxidation states of a transition metal within the same discrete molecular unit. During the preparation of *p*-TPPTP(H)$_6$ cobalt complexes for use as supported hydroformylation catalysts via grafting of the phosphonic acid group to TiO$_2$, we discovered the unusual coordination chemistry of this versatile ligand. Our rationale for supporting *p*-TPPTP(H)$_6$ into silica or onto metal oxide surfaces is based on the possibility of constraining the geometry of phosphine metal complexes, which may lead to differences in selectivity and activity for important metal complex catalyzed organic transformations. Supported or "heterogenized" molecular catalysis continues to be an active area of research due to the interest in establishing correlations between homogeneous and heterogeneous catalysis.[5] Additionally, supporting a homogeneous catalyst has the advantages of ease of separation of catalyst and product while maintaining the activity and selectivity found in the solution phase analogue. One of us recently described a new method for grafting phosphonic acid functionalized rhodium and iridium 2,2′-bipyridine complexes onto in situ generated TiO$_2$ particles.[6] The covalently supported metal complexes were then used for the catalytic hydrogenation of aromatic ketones with excellent activity, no significant metal leaching, and good reuseability. Lin and co-workers have also exploited the phosphonic acid moiety as an anchoring group and reported the immobilization of a chiral phosphonic acid functionalized BINAP complex of ruthenium onto amorphous microporous zirconia.[7] The resulting chiral porous solid was then used for the catalytic asymmetric hydrogenation of ketones with high % ee.

Experimental Section

General Data. All reactions were conducted under dry, prepurified N$_2$ using standard Schlenk-line and catheter-tubing techniques

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10.1021/om060898m CCC: $37.00

unless otherwise stated. IR spectra were recorded on Mattson and Nicolet FT spectrometers. All ^{31}P NMR spectra were recorded on Varian Inova 400, Bruker DRX 400, Bruker AM-300, or Varian EM360/Anasazi spectrometers and referenced to external H_3PO_4.

Solvents were purified as follows: toluene (EM Science or Aldrich), distilled from Na/benzophenone; 2-propanol (Aldrich), THF (Acros), used as received.

Reagents and chemicals were obtained as follows: dicobalt octacarbonyl (Alfa Aesar or Acros), phenylphosphonic acid (Aldrich), $Ti(OPr)_4$ (Aldrich), used as received. $P(4-C_6H_4PO_3H_2)_3$ (*p*-TPPTP(H)$_6$),[3b] $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$,[8] and $Na[Co(CO)_4]$[9] were prepared according to the literature procedures.

$Co_6(CO)_3$(*p*-TPPTP)$_2$$(H_2O)_{24}\cdot 24H_2O$ (2). A Schlenk tube was charged with DI water (15 mL), toluene (15 mL), $Co_2(CO)_8$ (0.300 g, 0.879 mmol), *p*-TPPTP(H)$_6$ (0.155 g, 0.293 mmol), and a stir bar. The biphasic mixture was stirred for 3 days, during which time a yellow precipitate formed in the aqueous layer. The aqueous layer was separated via cannula, washed with toluene, and centrifuged (3500 rpm) to remove the solid, and the yellow supernatant was transferred to a Schlenk tube. The resulting yellow solution was stored at 5 °C for 2 weeks, after which time yellow crystals formed, which were collected by filtration and dried under oil-pump vacuum to give **2** (0.31 g, 46%). IR (KBr pellet): ν(CO) 2002 (s) cm^{-1}.

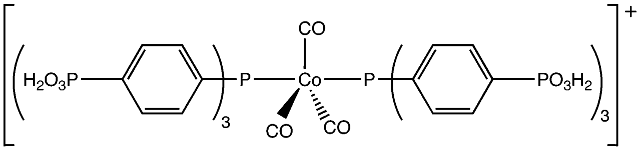
$Co_4(CO)_3$(*p*-TPPTP)$_2$$(H_2O)_{24}\cdot 24H_2O$ (3). A Schlenk tube was charged with DI water (10 mL), toluene (10 mL), $Co_2(CO)_8$ (0.296 g, 0.866 mmol), *p*-TPPTP(H)$_6$ (0.458 g, 0.866 mmol), and a stir bar. The biphasic mixture was stirred for 2 days, during which time a yellow precipitate formed in the aqueous layer. The organic layer was removed via cannula, and the remaining aqueous phase was washed with hexane (3 × 15 mL). The aqueous phase was then adjusted to pH 9 by dropwise addition of 2 M NaOH, which caused most of the precipitate to dissolve. Filtration via a cannula and filter stick gave a a clear red-orange solution. ^{31}P NMR analysis showed essentially a single phosphine complex at 54.2 ppm. The solution was then brought to pH 4−5 by careful addition of 2 M HCl and allowed to react with $Ti(OPr)_4$ as described below. Following separation of the sol−gel, complex **3** was recovered from the supernate (0.230 g) by concentration under oil-pump vacuum. IR (KBr pellet): ν(CO) 2075 (w), 2014 (s), 2000 (s), 1951 (m), 1933 (m) cm^{-1}. Crystals of **3** were obtained by dissolving approximately 50 mg of the isolated product in 0.5 mL water and layering with 0.5 mL of 2-propanol. After standing at room temperature for 5 days, the crystals suitable for XRD were collected and air-dried.

$[Co(CO)_3(PPh_3)_2][PhPO_3H]\cdot 3PhPO_3H_2$ (4). A Schlenk flask was charged with $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ (0.200 g, 0.239 mmol), phenylphosphonic acid (0.556 g, 2.52 mmol), THF (10 mL), and a stir bar. The solution was stirred for 24 h and the bright red solid $Co_2(CO)_6(PPh_3)_2$ removed by filtration. The orange filtrate was stored at 5 °C for 10 days, after which time yellow crystals formed, which were collected by filtration and dried under oil-pump vacuum to give **5** (0.063 g, 27%). IR (KBr pellet): ν(P−OH) 2800 (br, s), ν(CO) 1999 (s) cm^{-1}.

Synthesis of TiO_2-Supported Catalyst 5. A Schlenk flask was charged with a solution of **2** from the procedure described above and a stir bar. Then, $Ti(OPr)_4$ (1.4 mL, 4.7 mmol) was dissolved in 2-propanol (6.2 mL) and the solution added via syringe to the solution of **2** with rapid stirring. A cream-colored precipitate formed immediately upon addition. The reaction mixture was left stirring under N_2 for 12 h and then centrifuged (10 000 rpm) for 10 min. The cream-colored solid was washed with DI water (3 × 20 mL) and acetone (20 mL) and dried under oil-pump vacuum to give a tan solid (crude yield: 1.33 g). IR (KBr pellet), ν(CO) 2002 (s) cm^{-1}.

Results and Discussion

The biphasic disproportionation reaction of phosphine and $Co_2(CO)_8$ in H_2O/toluene was chosen as the method for coordination of *p*-TPPTP(H)$_6$ to cobalt. This reaction is well known and proceeds to give initially $[Co(CO)_3L_2][Co(CO)_4]$ (L = triarylphosphine), which rapidly decomposes to give the stable dimer $Co_2(CO)_6L_2$.[8] To our surprise, when the triarylphosphine *p*-TPPTP(H)$_6$ is used and the reaction is monitored by ^{31}P NMR, the cation **1** is formed exclusively in the aqueous phase, characterized by a single resonance at 56.0 ppm.[10] After stirring for 1 h a brown solid is formed, which on dissolving in 2 M NaOH shows, by ^{31}P NMR, the presence of the cation **1**, which is stable in solution under N_2 for at least 4 days. The in situ IR spectrum recorded immediately after commencement of the reaction shows an intense band at 2002 cm^{-1}, which can be attributed to the cation **1** as well as a weak band at 1930 cm^{-1} assigned to the anion $[Co(CO)_4]^-$, which disappears after 1 h.[11] The unusual behavior of *p*-TPPTP is in stark contrast to that of the water-soluble phosphine *m*-TPPTPS (*m*-triphenylphosphine trisulfonate), which yields predominantly $Co_2(CO)_6$(*m*-TPPTS)$_2$ under similar reaction conditions.[12]



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During the biphasic exchange reaction the ^{31}P NMR resonance at 14.7 ppm corresponding to the phosphonic acid group quickly broadens, eventually disappearing into the baseline. We suspected that this was due to simultaneous oxidation of excess $Co_2(CO)_8$ to Co^{2+} at the toluene/water interface and coordination of the pendent phosphonate groups of **1** to the Co^{2+} center in the aqueous layer. To provide experimental support for this, an Evan's-type experiment was performed in which the chemical shift of an internal NMR reference (*t*-BuOH) was monitored over the course of the exchange reaction. An excellent correlation between phosphonate line width at half-height and increase in bulk magnetic susceptibility over time was observed. On standing at 5 °C for 2 weeks, crystals of **2** were collected from the aqueous phase. The ORTEP representation of **2** is shown in Figure 1 and shows some rather unusual features.

Compound **2** is a rare case of a mixed-valence Co(I)/Co(II) coordination complex and to the best of our knowledge is the first organometallic example. In addition, an unprecedented variety of structural motifs occur in this single complex.

The unit cell contains six crystallographically unique cobalt ions, one Co^+ ion that is present in the $[Co(CO)_3$(*p*-TPPTP)$_2]^+$ cation and five Co^{2+} ions, two of which show coordination of a single phosphonate ligand $[Co(H_2O)_5$(*p*-TPPTP)$]$, two ions that are coordinated in both *cis* and *trans* geometries to two phosphonates $[Co(H_2O)_4$(*p*-TPPTP)$_2]$, and one cobalt ion that is present as $[Co(H_2O)_6]^{2+}$. Charge assignments were made on the basis of reported metal−ligand bond lengths for complexes with known oxidation states, bond valence sum (BVS) analysis,[13] and geometrical considerations. A single phosphonate

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[10] On repeating this experiment many times, ocassionally a very minor unidentified peak has appeared at 67.0 ppm.

[11] Assignment of the IR band observed at 1930 cm^{-1} was confirmed using an independently prepared sample of $Na[Co(CO)_4]$.

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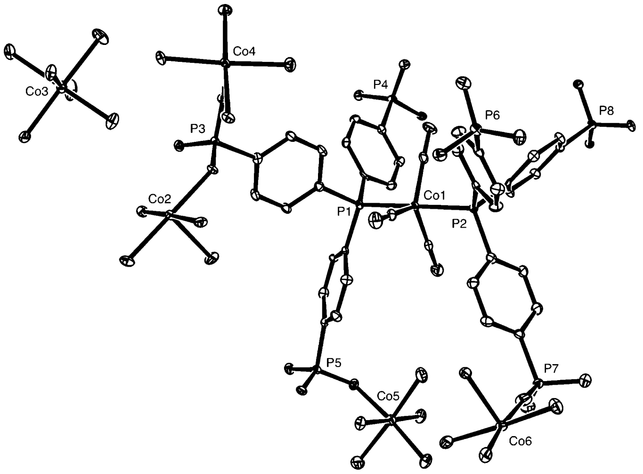

Figure 1. ORTEP representation of **2** (ellipsoids at 50% probability). Hydrogen atoms and solvate molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−P(1) = 2.229(1); Co(1)−P(2) = 2.221(1); Co(1)−C(1) = 1.795(5); Co(1)−C(2) = 1.798(5); Co(1)−C(3) = 1.799(6); P(1)−Co(1)−C(1) = 89.2(1); P(1)−Co(1)−C(2) = 91.6(1); P(1)−Co(1)−C(3) = 89.8(1); P(2)−Co(1)−C(1) = 88.5(1); P(2)−Co(1)−C(2) = 91.4(1); P(2)−Co(1)−C(3) = 89.6(1); C(1)−Co(1)−C(2) = 120.0(2); C(1)−Co(1)−C(3) = 121.8(2); C(2)−Co(1)−C(3) = 118.2(2).

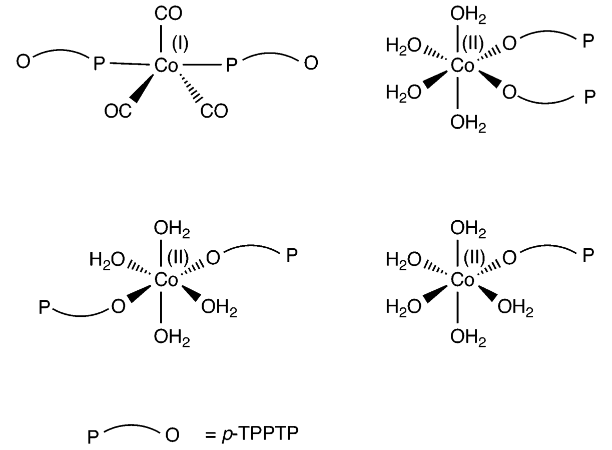

Figure 2. Structural motifs for TPPTP bonding found in **2**.

oxygen of the *p*-TPPTP ligand is protonated, which accounts for complete charge balance. The different coordination modes for *p*-TPPTP present in the unit cell of **2** are summarized in Figure 2.

Crystallization of an aqueous solution of **1** adjusted to pH 4.5 with 20% HCl and layered with 2-propanol yielded crystals of **3**, and the ORTEP representation is shown in Figure 3. In contrast to **2**, complex **3** contains four cobalt ions in the unit cell: the complex ion $[Co(CO)_3(TPPTP)_2]^+$ and three Co^{2+} ions, each of which is coordinated to a single oxygen of a phosphonate ligand. Thus by simply varying the pH of the aqueous solution of **1**, a different combination of binding motifs for the phosphonate ligand are obtained. It is also worth speculating that these supramolecular phosphonic acid complexes are molecular "snapshots" of model intermediates formed during the reaction of organophosphonic acids and metal salts to give layered metal organophosphonates, for which the mechanism is still poorly understood.

As mentioned previously, the redox chemistry that results in the formation of the supramolecular Co^+/Co^{2+} complexes is likely to result from water-promoted disproportionation of cobalt octacarbonyl at the toluene/water interface.[14] All reactions were performed with the rigorous exclusion of air, and yet the formation of Co^{2+} is rapid and reproducible. When water is excluded from the reaction and replaced with an organic solvent in the presence of a simple organophosphonic acid, oxidation to Co^{2+} and subsequent coordination of a phosphonate ligand does not occur. For example, the reaction of an authentic sample of $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ with phenylphosphonic acid in anhydrous THF does not result in oxidation to Co^{2+}, but yields crystals of $[Co(CO)_3(PPh_3)_2][PhPO_3H]{\cdot}3PhPO_3H_2$ (**4**) (Figure 4) and the dimer $Co_2(CO)_6(PPh_3)_2$.[8]

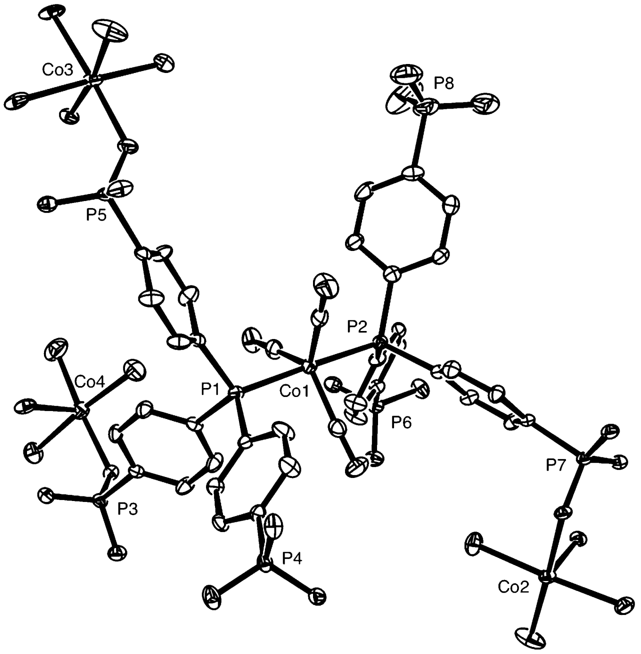

Figure 3. ORTEP representation of **3** (ellipsoids at 50% probability). Hydrogen atoms and solvate molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−P(1) = 2.243(9); Co(1)−P(2) = 2.239(1); Co(1)−C(1) = 1.820(4); Co(1)−C(2) = 1.807(4); Co(1)−C(3) = 1.808(4); P(1)−Co(1)−C(1) = 92.0(1); P(1)−Co(1)−C(2) = 88.7(1); P(1)−Co(1)−C(3) = 89.6(1); P(2)−Co(1)−C(1) = 91.2(1); P(2)−Co(1)−C(2) = 89.2(1); P(2)−Co(1)−C(3) = 89.5(1); C(1)−Co(1)−C(2) = 119.1(2); C(1)−Co(1)−C(3) = 117.0(2); C(2)−Co(1)−C(3) = 123.9(2).

Furthermore, the reaction of $Co_2(CO)_8$ and phenylphosphonic acid under aqueous biphasic conditions (H_2O/toluene) results in exclusive formation of the previously reported layered cobalt(II) phenylphosphonate,[15] supporting our contention that oxidation is water mediated.

Using the methodology previously reported by one of us,[6] cation **1** was covalently bonded to TiO_2 particles that were generated in situ via hydrolysis of titanium tetraisopropoxide, which after washing with water and acetone gives the supported cobalt phosphine species **5**, which has a Co loading of 2.5 wt % and a measured surface area of 88 m^2/g (cf. 94 m^2/g for the related TiO_2-supported rhodium bipyridine hydrogenation catalyst[1]). Solid-state ^{31}P NMR and IR spectroscopy of **5** confirmed the presence of the cation **1** as the only cobalt carbonyl/phosphine species present, and XPS studies confirmed both the presence of Co(I) and *absence* of Co(II). Presumably any discreet anions associated with cation **1** are removed during the washing stage of the workup. Supported complex **5** is a pale yellow solid when dry, which gradually decomposes in air. Interestingly,

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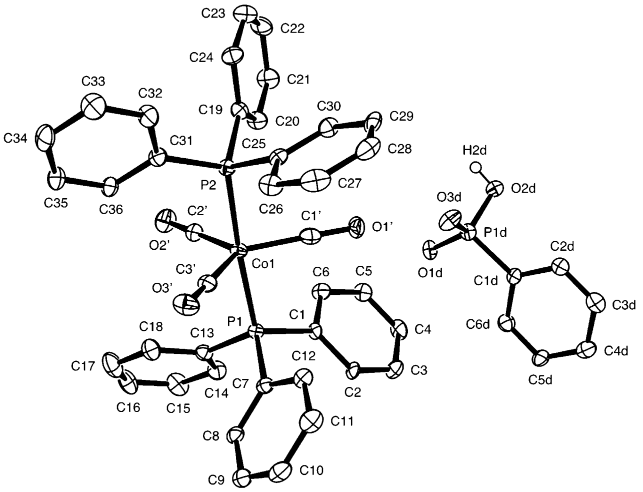

Figure 4. ORTEP representation of **4** (ellipsoids at 50% probability). Hydrogen atoms and solvate molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−P(1) = 2.2523(6); Co(1)−P(2) = 2.2405(6); Co(1)−C(1′) = 1.785(2); Co(1)−C(2′) = 1.791(2); Co(1)−C(3′) = 1.785(2); P(1)−Co(1)−C(1′) = 89.00(6); P(1)−Co(1)−C(2′) = 92.09(7); P(1)−Co(1)−C(3′) = 90.73(7); P(2)−Co(1)−C(1′) = 88.05(6); P(2)−Co(1)−C(2′) = 91.40(7); P(2)−Co(1)−C(3′) = 88.77(7); C(1′)−Co(1)−C(2′) = 122.0(1); C(1′)−Co(1)−C(3′) = 121.6(1); C(2′)−Co(1)−C(3′) = 116.4(1).

when exposed to moisture, **5** undergoes a color change from yellow to emerald green, which is completely reversible; that is, when water is removed by oil-pump vacuum, the yellow color of **5** returns. We suspected that this water-induced solvatochromism is redox in nature and was confirmed by a XPS of the green solid **6**, which indicated the presence of Co^{2+}. We are currently investigating the nature of this redox process in detail.

The XPS results and graphical fitting results for the Co $2p_{3/2}$ peak are shown in the waterfall plot in Figure 5. The $Co(CO)_3(PPh)_3^{2+}$ standard for Co(I) has a single peak at 781.9 ± 0.1 eV. Similarly compound **5** (Figure 5b) has a similar peak at 781.8 ± 0.1 eV, confirming that this is also a Co(I) compound. The results for the oxidized compound **6** (Figure 5c) show the expected Co $2p_{3/2}$ peak near 782.9 ± 0.1 eV for known Co(II) compounds plus a "shake up" or satellite peak above the $2p_{3/2}$ transition.[16] The satellite peak creates a clear delineation between Co(I) and Co(II) (or even Co(III) and Co(0)[17] compounds). Satellite peaks are caused by the charge transfer that occurs when an electron is ejected from the 3d orbitals of transition metal 2p ligands, but do not occur when the orbitals are filled, as in a Co(I) phosphine $3d^8$ compound.

Our survey of the XPS literature found no reports on the presence or absence of satellite peaks of Co(I), but analogous compounds such as Cu(I) in Cu_2O,[18] which has a $3d^{10}$ electron configuration, have no satellite structure. Thus, the XPS of the single Co peak in Figures 5a and 5b can be accurately ascribed to a Co(I) compound.

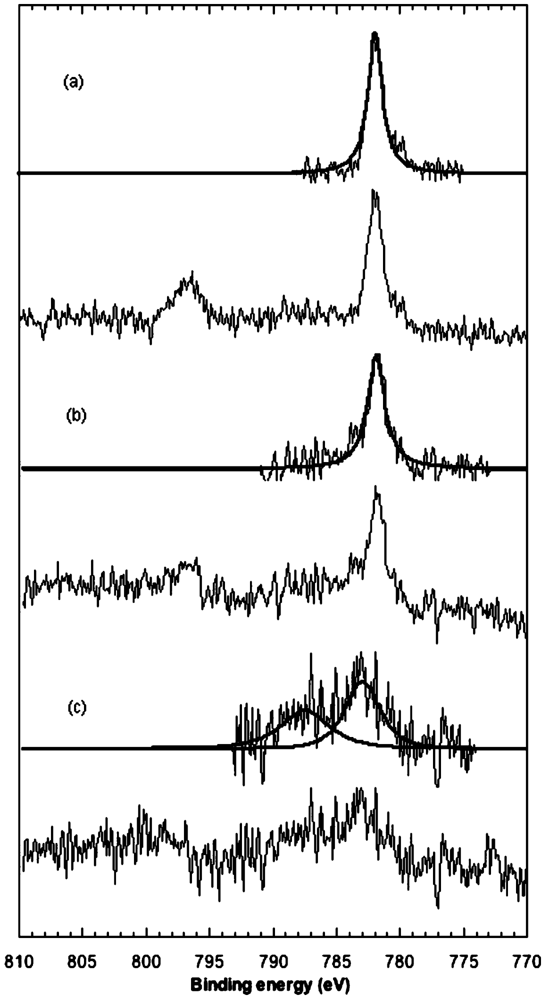

Figure 5. XPS of Co 2p region for (a) $[Co(CO)_3(PPh_3)_2]^+$; (b) compound **5**; (c) compound **6**. Top: Co $2p_{3/2}$ fit; bottom: full spectrum.

Preliminary tests on the activity of **5** in the hydroformylation of 1-octene indicated that the material has similar activity to other supported cobalt-based hydroformylation catalysts, but the selectivity is somewhat different. In a typical reaction run at 800 psi and 155 °C, a 26% conversion to aldehydes with an *n*/*i* ratio of 0.57 was observed. Only a trace of alcohol was detected.[18] Unmodified cobalt catalysts give *n*/*i* ratios of 1.4−4.4, and phosphine-modified systems usually show even higher *n*/*i* ratios.[19] The low conversion to alcohol (hydrogenation activity) is more typical of unmodified cobalt catalyst compared with phosphine-modified systems, which produce high yields of alcohol product.[20] The effects of reaction temperature, pressure, and quantity of catalyst variables on the overall aldehyde yield were evaluated using a 2^3-factorial statistical design method,[21] as summarized in the Supporting Information. The results indicate that the overall yield of aldehydes is slightly favored by increased pressure and significantly disfavored by higher temperatures, suggesting possible catalyst decomposition at higher temperatures. Loss of cobalt to the organic phase varied from 1 ppm (at 800 psi/155 °C) to 3 ppm (at 1200 psi/195 °C).

These values are either similar or lower than those typically observed for immobilized cobalt catalysts (either solid-supported, aqueous biphasic, or ionic liquid reaction conditions).[22−25]

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The supported catalyst was recycled with very little loss of activity. Under biphasic conditions (**1**, H_2O/toluene), a reversal of the *n*/*i* ratio was observed (1.30−1.09), which is more typical of homogeneous phosphine-modified catalyst. The lack of any hydroformylation activity of the unsupported complex **2** suggests that the supporting TiO_2 framework is required for catalytic activity. The low level of cobalt leaching from **5** into the organic phase points to a “ligand-supported” rather than homogeneous catalyst. We are currently investigating the mechanism of the “heterogenized” catalyst using in situ IR, and our results will be published in due course.

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Supporting Information Available: Details of XPS experiments, hydroformylation studies, and crystallographic data in the form of CIF files for compounds **2**−**4**. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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