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An Extension of the Wittig Reaction: Attack of Phosphorus Ylides at Acyl Groups in Organocobalt Complexes

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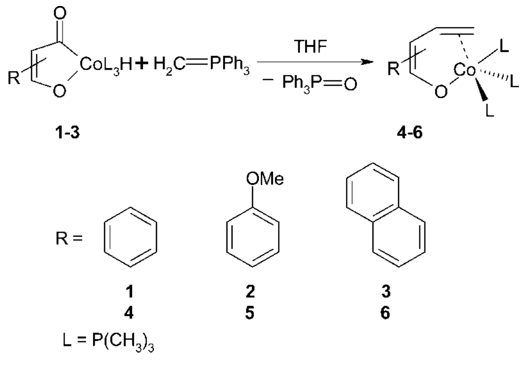
Attack of phosphorus ylides at acyl groups in organocobalt complexes was observed. Reactions of hydrido(acylenolato) cobalt(III) complexes [Co^{III}(O∩CO)L_3H] (O∩CO = acylenolato ligand, L = $P(CH_3)_3$) **1**–**3** with phosphorus ylides ($H_2C{=}PPh_3$, $H_2C{=}P(n\text{-Bu})_3$, $CH_3CH{=}PPh_3$) afford eight novel organocobalt compounds. The structures of the eight compounds greatly differ according to the electronic and steric properties of the reactants. As a result of the Wittig reaction compounds [Co^{I}(O∩=)L_3], **4**–**6** and **9** are (π-olefin)cobalt(I) compounds. Compound [Co^{II}(O∩CO)L_3] **8** is a stable (acylenolato)cobalt(II) complex with 17 valence electrons. The dinuclear compounds [Co^{II}(O∩CO)L_2]$_2$ **10**–**12** show unusual properties, as they are diamagnetic in solid state and possess centrosymmetric structures containing a [Co(μ_2-O)]$_2$ ring, while in solution they are mononuclear and paramagnetic. The crystal structures of the compounds **4**–**6**, **8**, **9**, and **11** were determined by X-ray diffraction. The mechanisms of formation are discussed.

Introduction

The Wittig reaction is the most useful method for transformation of carbonyl compounds into alkenes in organic synthesis.[1] In recent years, the Wittig reaction involving organometallic compounds has received much attention.[2–8] Wright et al. reported the first example of a Wittig reaction on carbon dioxide when π-coordinated in a nickel complex achieving olefination of carbon dioxide.[5] A convenient synthesis of bimetallic alkenyl complexes via Wittig reaction was studied.[7] Lee et al. reported an olefination reaction of aldehydes and ketones catalyzed by a cobalt(II) porphyrin complex, and results showed that the high-yield reaction was also highly selective.[9] Phosphorus ylides attack the bridging carbonyl ligand in [$Ni_2(\mu_2\text{-CO})(CO)_2$(dppm)] (dppm = bis(diphenylphosphino)methane) to form μ-alkylidene complexes in a C−C coupling reaction.[10] However, few examples of this type of reaction have been reported with organocobalt complexes to our knowledge. Furthermore, up to now no direct Wittig reaction of phosphorus ylides with an acylmetal group was reported. In our present work, we have employed three phosphorus ylides with different alkyl groups on phosphorus and carbon atoms and studied their reactions with five hydrido(acylenolato)cobalt(III) complexes under mild conditions. Eventually, three types of product were obtained due to the different substituents in the ligand backbone of the hydrido(acyl)enolatocobalt(III) complexes and in the phosphorus ylides. For the first time, π-olefin cobalt complexes were prepared using a Wittig reaction. Dinuclear (acylenolato)cobalt complexes were also obtained via a Wittig reaction.

Results and Discussion

1. Reaction of Hydrido(acyl)enolatocobalt(III) Complexes (1–3) with $Ph_3P{=}CH_2$. The reaction of $H_2C{=}PPh_3$ with compounds **1**−**3** in THF at room temperature gave rise to three novel (π-olefin)cobalt complexes **4**–**6** (eq 1).



(1)

Complexes **4**–**6** were obtained as dark red crystals in high yields by crystallization at −30 °C. Crystals of **4**–**6** remain stable at room temperature for more than 3 h but quickly decompose when dissolved and exposed to air.

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(1) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, 863. (b) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (c) Cristau, H. J. *Chem. Rev.* **1994**, *94*, 129.

(2) King, R. B.; Wu, F. J.; Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449.

(3) King, R. B.; Wu, F. J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764.

(4) King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *Inorg. Chem.* **1991**, *30*, 1174.

(5) Wright, C. A.; Thorn, M.; McGill, J. W.; Sutterer, A.; Hinze, S. M.; Prince, R. B.; Gong, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 10305.

(6) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1999**, *18*, 582.

(7) Liu, S. H.; Xia, H.; Wan, K. L.; Yeung, R. C. Y.; Hu, Q. Y. *J. Organomet. Chem.* **2003**, *683*, 331.

(8) Obendorf, D.; Schottenberger, H.; Wurst, K.; Schuler, N.; Laus, G. *J. Organomet. Chem.* **2005**, *690*, 811.

(9) Lee, M. Y.; Chen, Y.; Zhang, X. P. *Organometallics* **2003**, *22*, 4905.

(10) Wright, C. A.; Thorn, M.; McGill, J. W.; Sutterer, A.; Hinze, S. M.; Prince, R. B.; Gong, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 10305.

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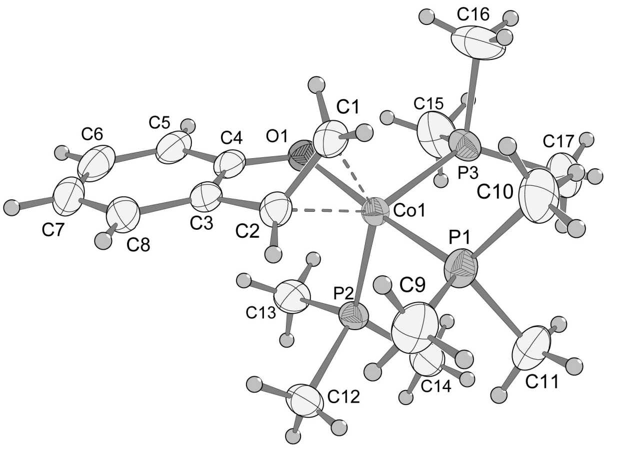

Figure 1. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): C1−C2 1.433(3), C1−Co1 1.9967(19), C2−Co1 2.025(2), Co1−O1 1.9972(13), Co1−P1 2.1633(6), Co1−P3 2.2191(6), Co1−P2 2.2414(6); O1−Co1−P1 174.63(4), C1−Co1−P1 88.02(6), C2−Co1−P1 94.72(6), O1−Co1−P3 83.93(4), P1−Co1−P3 95.68(2), O1−Co1−P2 87.53(4), C2−Co1−P2 102.94(6), P1−Co1−P2 97.71(2), P3−Co1−P2 106.03(2).

In the IR spectra of compounds **4**−**6**, the Co−H bands of starting materials (**1**−**3**) have disappeared. In the ^{1}H NMR spectra, signals of the three olefinic protons are recorded between 2.17 and 4.72 ppm. This observation indicates that the Wittig reaction has occurred at the (C═O) bond of the acyl group of the hydrido(acyl)enolatocobalt(III) complexes **1**−**3**. In addition, the three trimethylphosphine ligands show broad signals (0.37, 1.04, 1.22 ppm) for **4**, doublets (0.38, 1.05, 1.25 ppm) for **5**, and broad signals (0.55, 1.04, 1.36 ppm) for **6**. These data indicate a trigonal bipyramidal geometry as expected,[11] which is proved by the ^{31}P NMR. At room temperature, three broad resonances are recorded for **4** (10.75, 12.98, 31.30 ppm), for **5** (12.99, 14.20, 31.50 ppm), and for **6** (13.66 (2P), 31.11 ppm (1P)). The olefinic carbon atoms were assigned by ^{1}H−^{13}C COSY NMR. Multiplets were found for compounds **4**−**6**: 40.2 and 58.9 ppm for **4**, 40.0 and 58.8 ppm for **5**, and 39.8 and 54.9 ppm for **6**. Their high-field shift, relative to those of normal olefins, arises from the strong π-backbonding of cobalt-3d electrons into the empty π^*-olefin orbitals. All spectral data obtained from solutions of **4**−**6** are consistent with the results of three X-ray diffraction experiments. The molecular structures of **4**−**6** are shown in Figures 1–3.

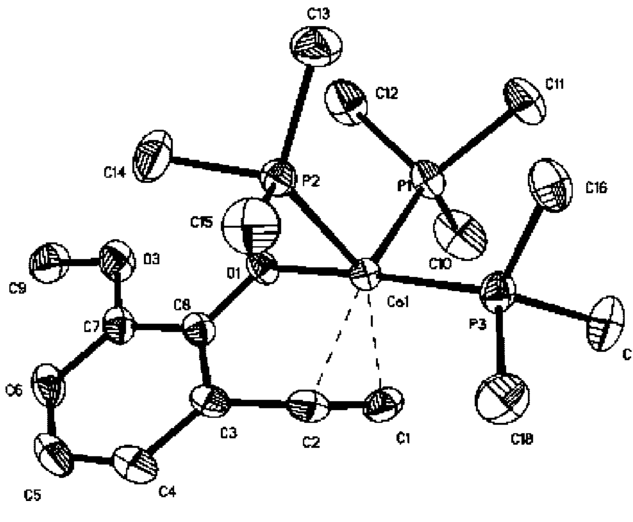

Figure 2. Molecular structure of **5** (all of the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): C1−C2 1.427(5), Co1−O1 1.9974(18), Co1−C1 1.999(3), Co1−C2 2.030(3), Co1−P3 2.1522(9), Co1−P1 2.2241(10), Co1−P2 2.2372(9); O1−Co1−C1 86.98(11), O1−Co1−C2 82.41(11), C1−Co1−C2 41.47(14), O1−Co1−P3 173.22(6), C1−Co1−P3 87.86(10), C2−Co1−P3 96.59(9), O1−Co1−P1 81.99(6), C1−Co1−P1 110.57(11), C2−Co1−P1 148.61(10), P3−Co1−P1 95.73(3), O1−Co1−P2 89.41(6), C1−Co1−P2 143.15(11), C2−Co1−P2 101.72(10), P3−Co1−P2 97.36(4), P1−Co1−P2 105.18(4).

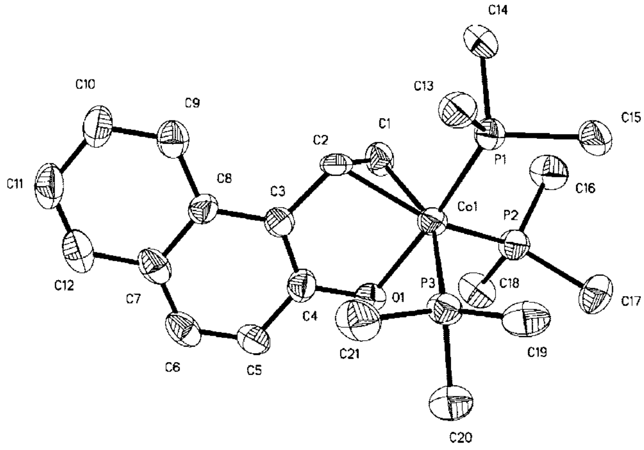

Figure 3. Molecular structure of **6** (all of the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): C1−C2, 1.420(15), Co1−C1 1.940(11), Co1−O1 1.990(8), Co1−C2 2.061(12), Co1−P1 2.150(4), Co1−P2 2.218(4), Co1−P3 2.232(4); C1−Co1−O1 85.7(4), C1−Co1−C2 41.5(4), O1−Co1−C2 82.5(4), C1−Co1−P1 95.9(4), O1−Co1−P1 168.7(3), C2−Co1−P1 91.2(4), C1−Co1−P2 95.9(4), O1−Co1−P2 91.7(3), C2−Co1−P2 137.2(4), P1−Co1−P2 99.21(14), C1−Co1−P3 153.6(4), O1−Co1−P3 80.3(2), C2−Co1−P3 114.0(4), P1−Co1−P3 93.83(14), P2−Co1−P3 106.69(15).

In the crystal structure of compound **4**, the cobalt atom is penta-coordinate in a trigonal bipyramidal geometry (TBP), two phosphrus atoms of the trimethylphosphine ligands and the (C═C) group occupy the equatorial positions, and the axial positions are taken by the phosphrous atom of the third trimethylphosphine ligand and the oxygen atom of the phenoxy group. The angle C1−Co1−C2 with 41.75(8)° is a little bit smaller than that (41.83°) of the compound (2-(η^2-2-propenoyl) benzo(*e*)cyclohexenolato)tris(trimethylphosphine)cobalt(I) reported by Klein.[11] The cobalt atom deviates by 0.1279 Å from the plane defined by atoms P2, P3, and the midpoint C1−C2. The axial angle O1−Co1−P1 is 174.63°; thus, the coordination at the Co shows a distorted TBP geometry. The angle between the vector C1−C2 and the plane [Co1, P2, P3] is only 7.8°, indicating that C1−C2 is almost in the plane [Co1, P2, P3]. The C1−Co1 bond (1.9967(19) Å) is a little bit shorter than that of the C2−Co1 bond (2.025(2) Å). The length of the bond C1−C2 is 1.433 Å, which is a little bit shorter than that (1.452 Å) of the compound reported by Klein[11] but substantially longer than expected for a carbon−carbon double bond (1.37 Å) due to strong back-bonding. The Co1−P1 distance (2.1633(6) Å) is a little bit shorter than Co1−P2 (2.2414(6) Å) and Co1−P3 (2.2191(6) Å), which is caused by the weak trans influence of the phenoxy-O atom.

Compounds **5** and **6** adopt a similar molecular structure. The axial angles are 173.22(6)° (O1−Co1−P1) in (**5**) and 168.7(3)° (O1−Co1−P1) in (**6**), indicating distorted TBP geometries. The

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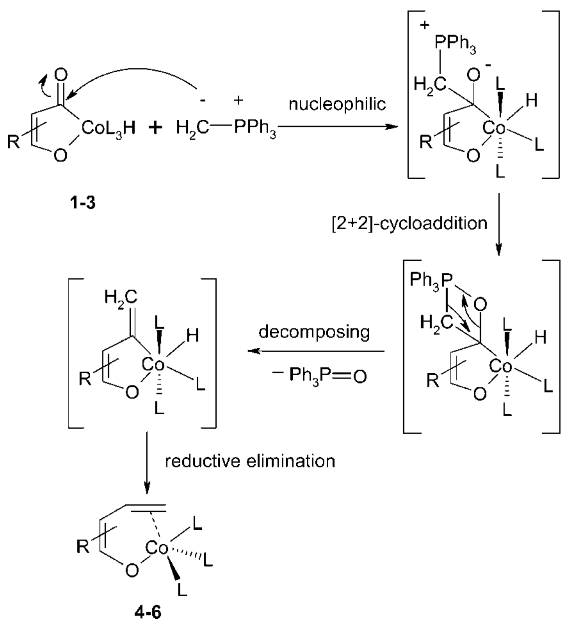
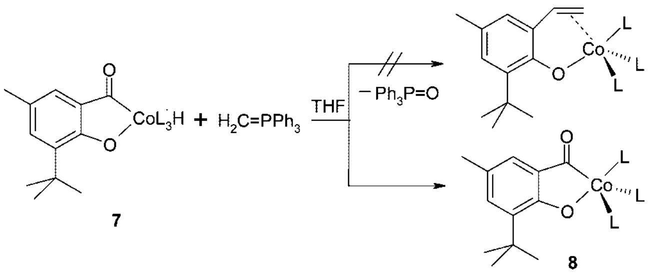
[11] Klein, H. F.; Li, X.; Floerke, U.; Haupt, H. J. *Z. Naturforsch. Teil B* **2000**, *55*, 707.

Scheme 1



Scheme 2



order of deviations from linearity (**6** > **5** > **4**) corresponds with the dimensions of the chelate ligands (naphthyl > methoxyphenyl > phenyl).

A likely formation mechanism of compounds **4**–**6** is presented in Scheme 1. As in the classic Wittig reaction by nucleophilic attack of the negatively charged carbon atom of the phosphorus ylide at the carbon atom of the acylcobalt group an oxaphosphetane intermediate is formed. Elimination of triphenylphosphine oxide leaves a σ-vinylcobalt hydride, which is not stable and through reductive elimination gives rise to the π-olefin cobalt(I) complexes **4**–**6** as final products.

When a reaction of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**7**) with $Ph_3P{=}CH_2$ was carried out under the same conditions, an (acylphenolato)cobalt(II) complex (**8**) (Scheme 2) was isolated and no product of a Wittig reaction as in eq 1 was found.

In IR spectra, the Co−H band has disappeared, and a new strong band at 1598 cm^{-1} is found, which is assigned to a C−O stretching frequency. Compound **8** is paramagnetic. An single-crystal X-ray diffraction was carried out (Figure 4).

In the molecular structure of compound **8**, the cobalt atom is pentacoordinate in a tetragonal pyramidal geometry. The basal plane is defined by two phosphorus atoms (P1 and P3) of the trimethylphosphine ligands, one oxygen atom (O1) of the phenoxy group and the carbon atom (C1) of the carbonyl group. The apical position is occupied by the third phosphorus atom (P2) of a trimethylphosphine ligand. The cobalt atom lies 0.5226 Å above the plane [O1, C1, P1, P2]. The sum of the angles around the cobalt in the basal plane is 355.68°, so the atoms Co1, O1, C1, P1, and P2 are almost coplanar.

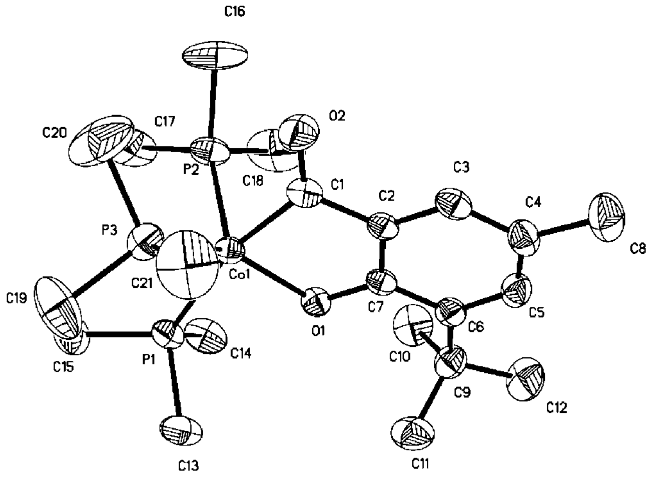
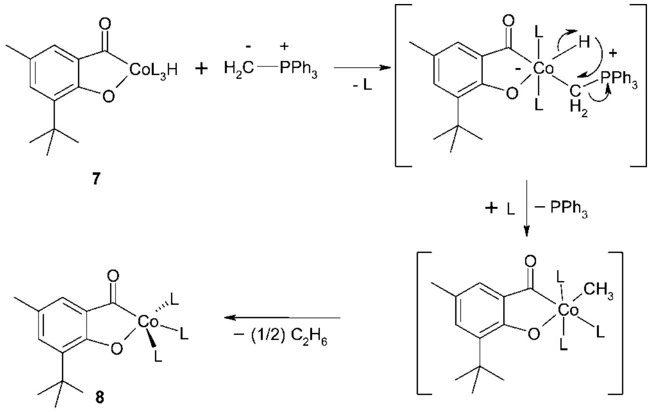


Figure 4. Molecular structure of **8** (all of the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): Co1−C1 1.918(4), Co1−O1 1.960(3), Co1−P3 2.2131(14), Co1−P2 2.2340(13), Co1−P1 2.3169(13), O2−C1 1.241(4); C1−Co1−O1 85.25(16), C1−Co1−P3 87.60(14), O1−Co1−P3 144.96(9), C1−Co1−P2 89.72(12), O1−Co1−P2 108.06(8), P3−Co1−P2 106.15(5), C1−Co1−P1 166.47(14), O1−Co1−P1 82.06(9), P3−Co1−P1 100.13(5), P2−Co1−P1 98.65(5).

Scheme 3



The proposed formation mechanism of compound **8** is shown in Scheme 3. Owing to the strong electronic donation and the steric crowding of the methyl and *tert*-butyl groups at the phenyl ring, the formation of an oxaphosphetane intermediate is unlikely. Instead, the phosphorus ylide as a nucleophile directly attacks the electron-deficient cobalt atom[12] and an ylide adduct is formed. The cobalt in this adduct is negatively charged, while the phosphorus atom bears a positive charge. This highly polar intermediate easily transforms into the methyl cobalt(III) complex with the release of triphenylphosphine. After an intermolecular elimination of ethane[13] and recoordination of the trimethylphosphine ligand, an (acylphenolato)cobalt(II) complex is formed as the end product (**8**).

2. Reaction of Hydrido(acyl)enolatocobalt(III) Complexes with $H_2C{=}P(n\text{-}Bu)_3$. Instead of $H_2C{=}PPh_3$, the smaller phosphorus ylide $H_2C{=}P(n\text{-}Bu)_3$ was used to investigate the influence of the alkyl groups upon this kind of Wittig reaction (eq

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[12] Karsch, H. H. Doctoral Thesis, Universitaet Wuerzburg, Germany, 1974.

[13] Yao, Z.; Wen, H.; Zha, Q.; Zhao, S. *J. Mass Spectrom.* **1996**, *31*, 955.

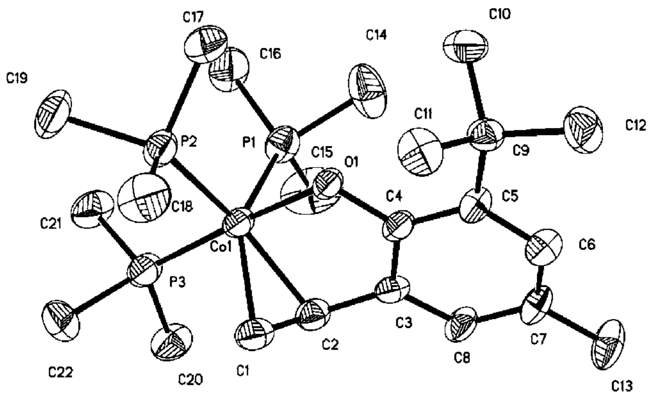
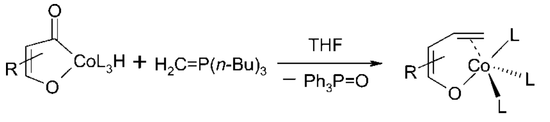


Figure 5. Molecular structure of **9** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): C1−C2 1.436(8), Co1−C1 1.998(6), Co1−O1 2.018(4), Co1−C2 2.032(6), Co1−P3 2.172(3), Co1−P2 2.221(3), Co1−P1 2.232(3); C1−Co1−O1 87.4(2), C1−Co1−C2 41.7(2), O1−Co1−C2 82.1(2), C1−Co1−P3 87.1(2), O1−Co1−P3 172.74(14), C2−Co1−P3 96.8(2), C1−Co1−P2 109.1(2), O1−Co1−P2 81.02(14), C2−Co1−P2 146.9(2), P3−Co1−P2 96.36(10), C1−Co1−P1 142.0(2), O1−Co1−P1 89.44(16), C2−Co1−P1 100.3(2), P3−Co1−P1 97.81(13), P2−Co1−P1 107.79(9).

2). Products (**4**−**6**) were characterized by IR and NMR spectra. Complexes **1**−**3** upon reaction with $H_2C{=}P(n\text{-}Bu)_3$ also afforded products (**4**−**6**) as with $H_2C{=}PPh_3$, while reaction of $H_2C{=}P(n\text{-}Bu)_3$ with **7** gave rise to a π-olefin complex **9** (similar to **4**–**6**). This reaction completely differs from that of **7** with $H_2C{=}PPh_3$. Obviously, the change of reaction mechanism is caused by the replacement of the Ph/*n*-Bu substituents at the phosphorus atom. The smaller size of the *n*-Bu groups renders an oxaphosphetane intermediate possible (Scheme 1). Compound **9** was studied by X-ray diffraction.



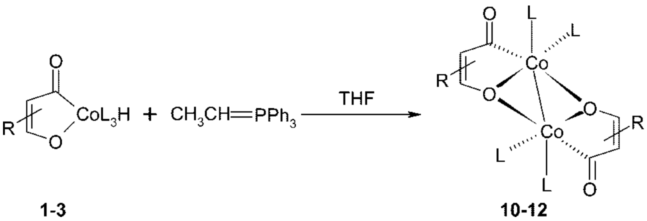
1-3, 7 **4-6, 9**

(2)

There are two independent molecules in the crystal cell of **9** that slightly differ in bond lengths and angles. One molecule is selected to describe the structure (Figure 5). The cobalt atom is pentacoordinate in a distorted TBP geometry, which is similar as that of **4**−**6**. The axial angle O1−Co1−P3 is 172.74(14)° fits in the order of spatial bulk of the substituents on the chelate ligands in **4**–**6** and **9**: naphthyl > 3-*tert*-butyl-5-methyl- > methyoxyphenyl > phenyl. The cobalt atom is located 0.5215 Å from the plane defined by O1, P1, P2 and the midpoint C1−C2.

3. Reaction of Hydrido(acyl)enolatocobalt(III) Complexes with $Ph_3P{=}CHCH_3$. Because size of both the substituents on phosphorus atom of the ylides and those on the backbone of the chelate ligand have great effect on the reaction mechanisms and products, an ethylidene function of $CH_3CH{=}PPh_3$ was introduced in order to learn more about this kind of Wittig reaction aiming at a stereoselective synthesis. To our surprise, three dinuclear cobalt (II) complexes were obtained as red crystals. No reaction products as with $H_2C{=}PPh_3$ or $H_2C{=}P(n\text{-}Bu)_3$ were observed.

In IR spectra, bands at 1609, 1607, and 1611 cm^{-1} for compounds **10**–**12**, respectively, are assigned to C=O groups.



1-3 **10-12**

(3)

Compound **11** was characterized by X-ray diffraction. The molecular structure is shown in Figure 6.

Compound **11** (Figure 6) contains centrosymmetric dinuclear molecules with two $[(3\text{-}CH_3O\text{-}2\text{-}OC_6H_3CO)Co(PMe_3)_2]$ moieties bonded via the two μ_2-O atoms of the phenoxy group and a short Co−Co σ-bond. The central $[Co(\mu_2\text{-}O)]_2$ ring has a "butterfly shape", which can be compared with the compound $[(Me_3Si)_3SiO]_2Co$ reported by Chesnokova.[14−19] The dihedral angle between the plane [Co1, O2, Co3] and the plane [Co1, O5, Co3] is 83.1° (the angle between the two wings of the butterfly). Each Co atom has a distorted octahedral geometry when each cobalt atom is considered coordinate to the other. Co1 atom deviates by 0.2062 Å from the plane [C1, O2, O5 and P2] toward the P4 atom. Such deviation is found for Co3 at 0.2047 Å toward P1 atom from the plane [C21, O2, O5 and P3]. The dihedral angle between the two planes ([C1, O2, O5 and P2] and [C21, O2, O5 and P3]) is 102.1°. The bridging Co−O bonds have an average distance of 2.018(±0.06) Å.

The Co1−Co3 distance with 2.4064(8) Å is significantly shorter than that of the compounds reported in the literature.[14−18] The diamagnetic properties in solid state (the magnetic susceptility is 0, which was experimentally confirmed) suggest the existence of a Co−Co σ-bond in the crystal, which is also present in **10** and **12**. But all three compounds are paramagnetic in solution. It is assumed that by solvation the centrosymmetric structure is cleaved into two independent paramagnetic molecules, while in the solid state spin-pairing is possible through metal−metal interactions.

The formation mechanism of compounds **10**–**12** (eq 3) is suggested in Scheme 4. The first step is a nucleophilic attack at cobalt to form an ylide adduct similar with that of **7** (Scheme 3). Transfer of the cobalt hydride to the carbon atom of the ylide affords an (1-triphenylphosphonio-1-ethyl)(acylphenolato) cobalt(III) complex, which is unstable and eliminates butane. A reaction mode as that of **7** with $CH_3CH{=}PPh_3$ did not occur. It is inferred that the substituents (3-*tert*-butyl and 5-methyl) on the chelate ligand hinder the nucleophilic attack of the ylide at the carbonyl group.

Conclusion

The reactions of three phosphorus ylides having different alkyl groups (different steric hindrance) with four hydrido(acyl)eno-

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(14) Chesnokova, T. T.; Zhezlova, E. V.; Kornev, A. N.; Fedotova, Y. V.; Zakharov, L. N.; Fukin, G. K.; Kursky, Y. A.; Mushtona, T. G.; Domrachev, G. A. *J. Organomet. Chem.* **2002**, *642*, 20.

(15) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *107*, 8087.

(16) Kornev, A. N.; Chesnokova, T. A.; Zhezlova, E. V.; Fukin, G. K.; Zakharov, L. N.; Domrachev, G. A. *Dokl. Akad. Nauk SSSR* **1999**, *369*, 203.

(17) Xu, Y.; Kang, B. K.; Chen, X.; Cai, Y.; Hu, Y.; Lu, J. *J. Cluster Sci.* **1992**, *3*, 167.

(18) Chen, Z. N.; Li, W. J.; Kang, B. S.; Hong, M. C.; Zhou, Y. Z.; Mark, T. C. W.; Lin, Z.; Chen, X. M.; Liu, H. Q. *Inorg. Chem.* **1997**, *36*, 208.

(19) Brechin, E. K.; Harris, S. G.; Parsons, S.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3403.

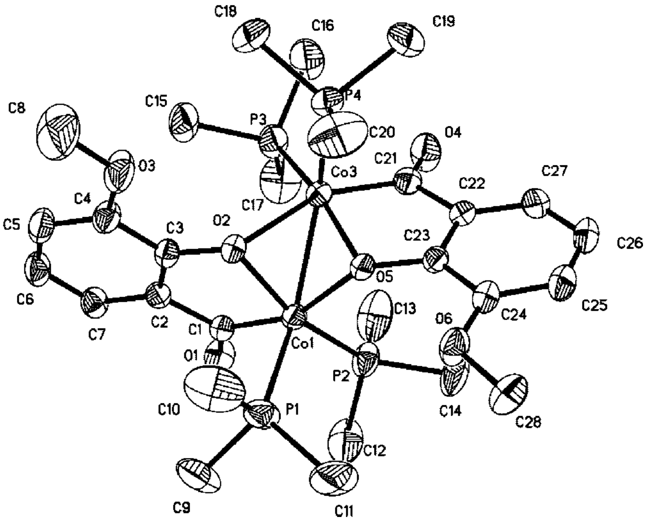
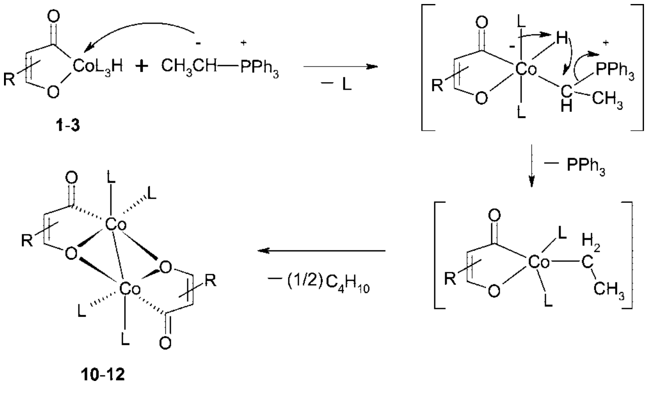


Figure 6. Molecular structure of **11** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): Co1−O2 1.963(3), Co1−O5 2.077(3), Co1−P2 2.1862(15), Co1−P1 2.2397(15), Co1−Co3 2.4064(8), Co3−C21 1.864(5), Co3−O5 1.974(3), Co3−O2 2.059(3), Co3−P3 2.1867(15), Co3−P4 2.2443(15); C1−Co1−O2 87.56(16), C1−Co1−O5 159.17(16), O2−Co1−O5 73.87(11), C1−Co1−P2 92.37(15), O2−Co1−P2 162.84(10), O5−Co1−P2 102.59(8), C1−Co1−P1 91.86(13), O2−Co1−P1 95.43(9), O5−Co1−P1 99.09(8), P2−Co1−P1 101.72(7), C1−Co1−Co3 109.86(13), O2−Co1−Co3 55.12(8), O5−Co1−Co3 51.60(7), P2−Co1−Co3 109.23(5), P1−Co1−Co3 140.82(5), C21−Co3−O5 87.14(16), C21−Co3−O2 157.40(16), O5−Co3−O2 74.04(11), C21−Co3−P3 92.01(15), O5−Co3−P3 165.55(9), O2−Co3−P3 103.08(9), C21−Co3−P4 94.57(15), O5−Co3−P4 94.34(9), O2−Co3−P4 99.14(9), P3−Co3−P4 100.10(6), C21−Co3−Co1 107.47(14), O5−Co3−Co1 55.55(8), O2−Co3−Co1 51.44(8), P3−Co3−Co1 111.33(5), P4−Co3−Co1 140.33(5).

Scheme 4



latocobalt(III) complexes were investigated under mild conditions, giving rise to three types of products. It was found that both the substituents on the chelate ligands of the hydrido(acylenolato)cobalt(III) complexes and those of the phosphorus ylides display large steering effects. With small *n*-Bu substituents the products are (*π*-olefin)cobalt compounds **4**−**6** and **9**. The reactions of more bulky $CH_3CH{=}PPh_3$ with hydrido(acylenolato)cobalt(III) complexes **1–3** delivered the dinuclear cobalt compounds **10**−**12**. No reaction of compound **7** with $CH_3CH{=}PPh_3$ was observed. The reactions of $H_2C{=}PPh_3$ with hydrido(acylenolato)cobalt(III) complexes **1–3** afforded (*π*-olefin)cobalt compounds **4–6**, while an (acylphenolato)cobalt(II) compound (**8**) was obtained by the reaction of $H_2C{=}PPh_3$ with **7**.

Experimental Section

General Procedures and Materials. All air-sensitive and volatile materials were handled either in vacuo or under argon by using standard Schlenk techniques. Phosphorus ylides[20] and hydrido(acylenolato)cobalt(III) complexes[21] were prepared by published procedures. Other chemicals were used as purchased. All solvents were dehydrated and degassed before use. IR: Nujol mulls between KBr disks, Bruker spectrophotometer type VECTOR 22. ^1H, ^{13}C, and ^{31}P NMR spectra (300, 75.4, and 121.4 MHz, respectively) were recorded with a Bruker AVANCE-300 spectrometer. For C, H analyses an automatic Elementar Vario ELIII analyzer was used.

Preparation of (η^2-2-Vinylphenoxy)tris(trimethylphosphine)cobalt(I) (4). Method A: A sample of *mer*-hydrido(2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**1**) (0.82 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}PPh_3$ (0.56 g, 2 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned dark red. The volatiles were removed in vacuo, and the resulting solid was extracted with ether (60 mL). Crystallization at −30 °C afforded dark red crystals 0.55 g (68%). Method B: A sample of *mer*-hydrido(2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (0.82 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}P(n\text{-}Bu)_3$ (0.43 g, 2 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 10 h. During this period, the reaction mixture turned dark red. The volatiles were removed in vacuo, and the resulting solid was extracted with ether (60 mL). Crystallization at −30 °C afforded dark red crystals 0.43 g (53%). IR (Nujol mull, 2600–1570 cm^{-1}): 1575s, *ν*(C=C). ^1H NMR (300 MHz, benzene-d_6, 297 K): *δ* 0.37 (d, $^2J(PH) = 4.8$ Hz, 9 H, PCH_3), 1.04 (br, 9 H, PCH_3), 1.22 (br, 9 H, PCH_3), 2.17 (br, 1 H, olefin-H), 2.59 (br, 1 H, olefin-H), 4.02 (br, 1 H, olefin-H), 6.66 (br, 1 H, aromatic-H), 7.04 (br, 1H, aromatic-H), 7.49 (br, 1H, aromatic-H), 7.73(br, 1H, aromatic-H). ^{13}C NMR (75.4 MHZ, benzene-d_6, 297 K): *δ* 18.2 (m, PCH_3), 18.8 (m, PCH_3), 19.3 (m, PCH_3), 40.2 (m, olefin-C), 58.9 (m, olefin-C), 111,9, 116.4, 122.8, 125.4, 142.7 (aromatic-C), 170.8 (O-C). ^{31}P NMR (121.4 MHz, benzene-d_6, 297 K): *δ* 10.75 (br, 1P, PCH_3), 12.98 (br, 1P, PCH_3), 31.3 (br, 1P, PCH_3). Anal. Calcd for $C_{17}H_{34}CoOP_3$: C, 50.25; H, 8.43. Found: C, 49.97; H, 8.50.

Preparation of (2-Methoxy-η^2-6-vinylphenoxy)tris(trimethylphosphine)cobalt(I) (5). Method A: A sample of *mer*-hydrido(3-methoxy-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**2**) (0.87 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}PPh_3$ (0.56 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as method A for **4**, dark red crystals **5** (0.58 g, 64%) were obtained. Method B: A sample of *mer*-hydrido(3-methoxy-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (0.87 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}P(n\text{-}Bu)_3$ (0.43 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as method B for **4**, dark red needles of **5** (0.50 g, 57%) were obtained. IR (Nujol mull, 2600–1570 cm^{-1}): 1576s, *ν*(C=C). ^1H NMR (300 MHz, benzene-d_6, 297 K): *δ* 0.38 (d, $^2J(PH) = 6.9$ Hz, 9 H, PCH_3), 1.05 (d, $^2J(PH) = 3.9$ Hz, 9 H, PCH_3), 1.25 (d, $^2J(PH) = 4.5$ Hz, 9 H, PCH_3), 2.18 (br, 1 H, olefin-H), 2.59 (br, 1 H, olefin-H), 3.71 (s, 3 H, OCH_3), 4.03 (br, 1 H, olefin-H), 6.54 (br, 1 H, aromatic-H), 6.75 (br, 1 H, aromatic-H), 7.23 (br, 1 H, aromatic-H). ^{13}C NMR (75.4 MHz, benzene-d_6, 297 K): *δ* 18.3 (m, PCH_3), 18.8 (m, PCH_3), 19.2 (m, PCH_3), 40.0 (m, olefin-C), 57.1 (s, OCH_3), 58.8 (m, olefin-C), 111.2, 112.7, 117.7, 144.2 (aromatic-C), 151.4 (O-CH_3), 160.4 (O-C). ^{31}P NMR (121.4 MHz, benzene-d_6, 297 K): *δ* 13.0 (br, 1 P, PCH_3),

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[20] Köster, V. R.; Simić, D. J.; Grassberger, M. A. *Liebigs Ann. Chem.* **1970**, *739*, 211.

[21] Klein, H. F.; Haller, S.; Sun, H.; Li, X.; Jung, T.; Roehr, C.; Floerke, U.; Haupt, H. J. *Z. Naturforsch. Teil B* **1998**, *53*, 587.

Table 1. Crystallographic Data for Complexes 4–6, 8, 9, and 11

	4	5	6	8	9	11
empirical formula	$C_{17}H_{34}CoOP_3$	$C_{18}H_{36}CoO_2P_3$	$C_{21}H_{36}CoOP_3$	$C_{21}H_{41}CoO_2P_3$	$C_{44}H_{88}Co_2O_2P_6$	$C_{42}H_{72}Co_3O_9P_6$
formula wt	406.28	436.31	456.34	477.38	952.82	1083.61
cryst dimens, mm^3	0.36 × 0.30 × 0.18	0.58 × 0.52 × 0.35	0.30 × 0.25 × 0.20	0.24 × 0.20 × 0.15		0.22 × 0.17 × 0.12
T, K	193(2)	293(2)	273(2)	273(2)	273(2)	273(2) K
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	*P*21/*c*	*P*2(1)/*n*	*Pbca*	*C*2/*c*	$P\bar{1}$	*C*2/*c*
a, Å	35.691(4)	9.949(2)	10.0801(9)	28.010(6)	9.451(11)	38.5884(18)
b, Å	15.7847(11)	16.612(3)	16.5116(16)	12.243(3)	17.04(2)	15.8081(7)
c, Å	15.0799(18)	13.851(3)	28.773(3)	18.168(4)	17.85(2)	17.5754(8)
α, deg	90	90	90	90	76.164(11)	90
β, deg	96.458(13)	98.94(3)	90	120.901(4)	90	96.865(2)
γ, deg	90	90	90	90	73.90	90
V, Å^3	8441.7(15)	2261.4(8)	4788.9(8)	5346(2)	2675(5)	10644.3(8)
Z	16	4	8	8	2	8
*D*c, g cm^{-3}	1.279	1.282	1.266	1.186	1.183	1.352
abs coeff, mm^{-1}	1.04	0.979	0.925	0.834	0.830	1.151
rflns collected	69308	9400	21578	9734	24645	48997
indep rflns	14758	3995	3987	5782	9344	9373
R_{int}	0.0321	0.0416	0.2119	0.0752	0.1992	0.1006
$\theta_{max,}$ deg	25.00	25.03	25.03	28.57	25.00	25.00
R_1 ($I > 2\sigma(I)$)	0.0294	0.0363	0.0867	0.0524	0.0611	0.0462
wR_2 (all data)	0.0740	0.0990	0.2853	0.1271	0.1309	0.1122

14.2 (br, 1 P, PCH_3), 31.5 (br, 1 P, PCH_3). Anal. Calcd for $C_{18}H_{36}CoO_2P_3$: C, 49.55; H, 8.31. Found: C, 49.20; H, 8.13.

Preparation of (η^2-1-Vinylnaphthalene-2-yloxy)tris(trimethylphosphine)cobalt(I) (6). Method A: A sample of *mer*-hydrido(2-oxo-1-naphthoyl)tris(trimethylphosphine)cobalt(III) (**3**) (0.93 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}PPh_3$ (0.56 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as method A for **4**, dark red crystals of **6** (0.58 g, 64%) were obtained. Method B: A sample of *mer*-hydrido(2-oxo-1-naphthoyl)tris(trimethylphosphine)cobalt(III) (0.87 g, 2 mmol) in 30 mL of THF was combined with $H_2C{=}P(n\text{-}Bu)_3$ (0.55 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as method B for **4**, dark red crystals of**6** (0.46 g, 50%) were obtained. IR (Nujol mull, 2600–1570 cm^{-1}): 1574s, ν(C=C). ^{1}H NMR (300 MHz, benzene-d_6, 297 K): δ 0.55 (br, 9 H, PCH_3), 1.04 (br, 9 H, PCH_3), 1.36 (br, 9 H, PCH_3), 2.38 (br, 1 H, olefin-H), 2.77 (br, 1 H, olefin-H), 4.72 (br, 1 H, olefin-H), 7.10 (br, 1 H, aromatic-H), 7.13 (br, 1 H, aromatic-H), 7.52 (br, 1 H, aromatic-H), 7.64 (br, 1 H, aromatic-H), 7.89(br, 1 H, aromatic-H), 8.56 (br, 1 H, aromatic-H). ^{13}C NMR (75.4 MHz, benzene-d_6, 297 K): δ 18.4 (m, PCH_3), 18.7 (m, PCH_3), 19.3 (m, PCH_3), 39.8 (m, olefin-C), 54.9 (m, olefin-C), 118.7, 121.1, 121.8, 124.8, 125.0, 126.2, 128.8, 131.5, 132.3 (aromatic-C), 174.2 (O-C). ^{31}P NMR (121.4 MHz, benzene-d_6, 297 K): δ 13.66 (br, 2 P, PCH_3), 31.1 (br, 1 P, PCH_3). Anal. Calcd for $C_{21}H_{36}CoOP_3$: C, 55.27; H, 7.95. Found: C, 55.03; H, 8.11.

Preparation of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(II) (8). A sample of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**7**) (1.2 g, 2.5 mmol) in 30 mL of THF was combined with $H_2C{=}PPh_3$ (0.7 g, 2.5 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned purple red. The volatiles were stripped in vacuo, and the resulting solid was extracted with pentane (60 mL). Crystallization at −30 °C afforded purple red crystals (0.25 g, 22%). IR (Nujol mull, 2600–1570 cm^{-1}): 1598 s, ν(C=O), 946 vs, ν(P−C). Anal. Calcd for $C_{21}H_{41}CoO_2P_3$: C, 52.83; H, 8.66. Found: C, 52.59; H, 8.73.

Preparation of (2-*tert*-Butyl-4-methyl-η^2-6-vinylphenoxy)tris(trimethylphosphine)cobalt(I) (9). A sample of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**7**) (1.2 g. 2.5 mmol) in 30 mL of THF was combined with $H_2C{=}P(n\text{-}Bu)_3$ (0.54 g, 2.5 mmol) in THF (20 mL) at −78 °C. After the same workup as method B for **4**, dark red crystals of **9** (0.77 g, 65%) were obtained. IR (Nujol mull, 2600–1570 cm^{-1}): 1619s, ν(C=C). ^{1}H NMR (300 MHz, benzene-d_6, 297 K): δ 0.51 (d, ^2J(PH) = 8.1 Hz, 9 H, PCH_3), 1.09 (d, ^2J(PH) = 5.4 Hz, 9 H, PCH_3), 1.40 (d, ^2J(PH) = 4.5 Hz, 9 H, PCH_3), 1.68 (s, 9 H, $C(CH_3)_3$), 2.28 (br, 1 H, olefin-H), 2.56 (br, 1H, olefin-H), 2.61 (s, 3 H, CH_3), 4.16 (br, 1 H, olefin-H), 7.06 (br, 1 H, aromatic-H), 7.31 (br, 1 H, aromatic-H). ^{13}C NMR (75.4 MHZ, benzene-d_6, 297 K): δ 17.9 (m, PCH_3), 18.5 (m, PCH_3), 19.6 (m, PCH_3), 20.7(s, CH_3), 29.7 (s, $(CH_3)_3$), 33.9 (s, $C(CH_3)_3$), 39.0 (m, olefin-C), 59.7 (m, olefin-C), 115.2, 117.9, 121.5, 123.1, 135.3, 142.1 (aromatic-C). ^{31}P NMR (121.4 MHz, benzene-d_6, 297 K): δ 14.97 (s(br), 2 P, PCH_3), 31.20 (s(br), 1 P, PCH_3). Anal. Calcd for $C_{22}H_{44}CoOP_3$: C, 55.46; H, 9.31. Found: C, 55.17; H, 9.44.

Preparation of Bis(μ_2-2-oxobenzoyl)bis(trimethylphosphine))-dicobalt(II) (10). A sample of *mer*-hydrido(2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**1**) (0.82 g, 2 mmol) in 30 mL of THF was combined with $CH_3CH{=}PPh_3$ (0.58 g, 2 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned dark red. The volatiles were removed in vacuo, and the resulting solid was extracted with ether (60 mL). Crystallization at −30 °C afforded dark red crystals (0.17 g, 13%). IR (Nujol mull, 2600–1570 cm^{-1}): 1607 s, ν(C=O), 945 vs, ν(P−C). Anal. Calcd for $C_{26}H_{44}$ $Co_2O_4P_4$: C, 47.14; H, 6.69. Found: C, 47.43; H, 6.55.

Preparation of Bis(3-methoxy-μ_2-2-oxobenzoyl)bis(trimethylphosphine))dicobalt(II) (11). A sample of *mer*-hydrido(3-methoxy-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**2**) (0.87 g, 2 mmol) in 30 mL of THF was combined with $CH_3CH{=}PPh_3$ (0.58 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as that for **10** ,dark red crystals of **11** (0.24 g, 17%) were obtained. IR (Nujol mull, 2600–1570 cm^{-1}): 1607 s, ν(C=O), 945 vs, ν(P−C). Anal. Calcd for $C_{28}H_{48}Co_2O_6P_4$: C, 46.55; H, 6.70. Found: C, 46.60; H, 6.65.

Preparation of Bis(μ_2-2-oxo-1-naphthoyl)bis(trimethylphosphine))dicobalt(II) (12). A sample of *mer*-hydrido(2-oxo-1-naphthoyl)tris(trimethylphosphine)cobalt(III) (**3**) (0.93 g, 2 mmol) in 30 mL of THF was combined with $CH_3CH{=}PPh_3$ (0.58 g, 2 mmol) in THF (20 mL) at −78 °C. After the same workup as that for **10**, dark red crystals of **12** (0.41 g, 26%) were obtained. IR (Nujol mull, 2600–1570 cm^{-1}): 1607 s, ν(C=O), 945 vs, ν(P−C). Anal. Calcd for $C_{34}H_{48}Co_2O_6P_4$: C, 51.40; H, 6.09. Found: C, 51.72; H, 6.01.

CCDC-649713 (**4**), CCDC-649714 (**5**), CCDC-649715 (**6**), CCDC-649716 (**8**), CCDC-649717 (**9**), and CCDC-649718 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12

Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

X-ray Structure Determinations

Intensity data were collected on a Bruker AXS SMART APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data for complexes **4–6**, **8**, **9**, and **11** are summarized in Table 1. The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Acknowledgment. We gratefully acknowledge support by NSF China (No. 20572062) and The Doctoral Program of the Ministry of Education of China (MOE) (Nos. 20050422010 and 20050422011).

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