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Phosphine–Alkene Ligands as Mechanistic Probes in the Pauson–Khand Reaction

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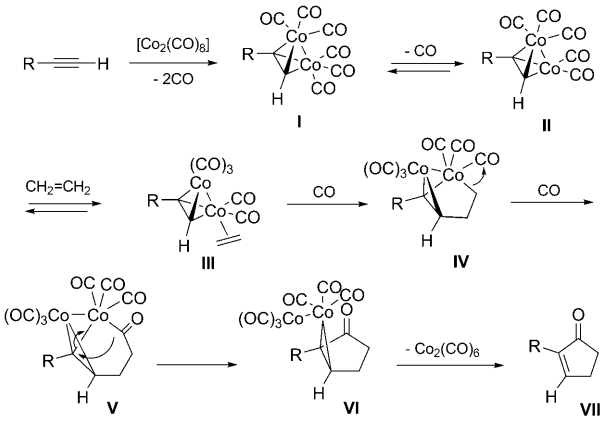
Dedicated to Prof. Santiago Olivella on the occasion of his 65th birthday

Abstract: An alkyne tetracarbonyl dicobalt complex with a chelated phosphine–alkene ligand, in which the phosphorus atom and the alkene from the ligand are attached to the same cobalt atom has been prepared, isolated, and characterized by X-ray crystallography. The complex serves as a mechanistic model for an intermediate of the Pauson–Khand (PK) reaction. Although the alkene fragment is located in an equatorial coordination site with an appropriate orientation, and, therefore, should undergo insertion, it failed to give the PK product upon either thermal or *N*-methylmorpholine *N*-oxide activation. However, a phosphine–alkene complex that contains a terminal alkene readily provided the corresponding PK product. We attribute this change in reactivity to the different ability of each olefin to undergo 1,2-insertion. These results provide further insights into the factors that govern a crucial step in the PK reaction, the olefin insertion.

Keywords: alkene ligands · cobalt · insertion · Pauson–Khand reaction · phosphane ligands

Introduction

The Pauson–Khand (PK) reaction is a cobalt-catalyzed or -mediated [2+2+1] cycloaddition of an alkyne, an alkene, and carbon monoxide to form a cyclopentenone.[1] It has been widely used to synthesize natural products containing a cyclopentane ring.[2,3] The commonly accepted mechanism of the PK reaction (Scheme 1) was originally proposed by Magnus.[4] The first step is the reaction of an alkyne unit and dicobalt octacarbonyl to form the hexacarbonyl complex **I**. Thermal activation yields loss of a CO molecule (**II**) and the resulting vacant position is occupied by an alkene (**III**). The alkene undergoes 1,2-insertion at the less hindered C–Co bond of the tetrahedral cluster. This is followed by coordination of a new CO molecule to form cobaltacycle **IV**, which undergoes CO insertion (**V**) and reductive elimination to give **VI**. Finally, reductive elimination of $[Co_2(CO)_6]$ affords the cyclopentenone **VII**.



Scheme 1. The Pauson–Khand reaction mechanism proposed by Magnus.

This mechanism is supported by theoretical studies performed by Nakamura,[5] Gimbert,[6] and Pericàs.[7] Nevertheless, little experimental evidence for the proposed inter-

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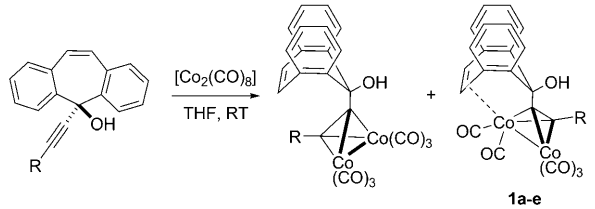
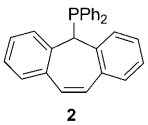
mediates has been found. In fact, of the intermediates that have been isolated and characterized, nearly all are of type **I**, although those of type **II** have been detected by IR spectroscopy,[8] and our group has isolated type **II** intermediates in reactions featuring an alkyne that contains a sulfur atom which can occupy the vacant coordination site.[9] Furthermore, one example of an intermediate of type **III** has been detected by electrospray ionization mass spectroscopy.[10] During failed attempts at inserting cyclopropene into Co_2–alkyne complexes, Fox et al. identified various side-products.[11] More recently, Evans and McGlinchey isolated and characterized (by X-ray diffraction) compounds **1a–e**, type **III** complexes in which an olefin is intramolecularly coordinated to a cobalt atom (Scheme 2).[12] Interestingly, complexes **1** do not undergo alkene insertion to give the corresponding PK adducts; the authors have attributed this lack of reactivity to two factors: the severe strain in the final PK adduct and the pseudoequatorial position of the alkene in complexes **1**.



1a: R= Ph; **1b**: R= TMS; **1c**: R= *p*-C_6H_4CN; **1d**: R= *p*-C_6H_4F; **1e**: R= *p*-$C_6H_4CF_3$

Scheme 2. Cobalt–alkene complexes characterized by Evans and McGlinchey; TMS = trimethylsilyl.

To determine if this lack of reactivity is, indeed, due to the relative orientations of the cobalt-coordinated alkyne and the alkene, and to gain mechanistic insights into the PK reaction, we decided to study the coordination and reactivity of phosphine–alkene ligands with alkyne–dicobalt complexes. We envisaged that phosphine–alkene ligands would be flexible enough to allow insertion of the olefin and would provide valuable information on the PK reaction mechanism. We chose two types of unsaturated phosphorous ligand: dibenzo[*a,d*]cyclohepten-5-yldiphenyl phosphine (**2**), the 5*H*-dibenzo[*a,d*]cycloheptene (suberene) substituent of which resembles complexes **1**; and the alkenyloxydiphenylphosphines **3**, featuring terminal alkenes. Herein, we report our study into the coordination and PK reactivity of alkyne dicobalt hexacarbonyl complexes with **2** and **3a–c**.



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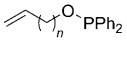
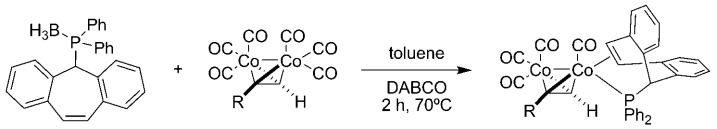


3a *n* = 1
3b *n* = 2
3c *n* = 3

Results and Discussion

Compound **2** is in the dibenzotropylidene phosphane (TROPP) class of ligands, which were originally described by Grützmacher et al.[13] We envisaged that once the phosphorus atom was coordinated to cobalt, the olefin moiety of the ligand would also be accessible for coordination. This, in turn, would enable olefin insertion, since the expected PK product would be less strained than those derived from complexes **1**. We observed better results using borane-protected **2** (**2-BH_3**) than if the free ligand was used. The free ligand was prepared by a slight modification of a literature procedure[13a] and was then treated with $BH_3{\cdot}SMe_2$ to form **2-BH_3**. In situ deprotection of **2-BH_3** with 1,4-diazabicyclo-[2.2.2]octane (DABCO, followed by reaction with the trimethylsilylacetylene dicobalt complex **4a** in toluene, at 70 °C, afforded a red solution, which was not isolated. After a further two hours, this complex yielded (as determined by TLC) complex **5a** (also red), which was isolated by chromatography in 42 % yield (Scheme 3). We obtained similar results for the reaction of **2-BH_3** with phenylacetylene complex **4b**.



2-BH_3

4a: R = TMS
4b: R = Ph

5a: R = TMS (42%)
5b: R = Ph (54%)

Scheme 3. The reaction of borane-protected **2** (**2-BH_3**) with acetylene dicobalt complexes.

We obtained suitable crystals of complex **5a** for analysis by X-ray diffraction (Figure 1).[14] The solid-state structure obtained unambiguously showed that the phosphorus atom and the alkene both coordinate to the same cobalt atom: the former is positioned pseudoaxially, whereas the latter occupies an equatorial coordination site *anti* to the TMS group. As in **1**, the seven-membered ring in **2** adopts a boat conformation, providing a characteristic avian-type structure. However, in sharp contrast to the case of **1**, described by Evans and McGlinchey,[12] coordination of **2** to the alkyne–dicobalt complex (**5a**) does not distort the ligand arrangement around the Co_2C_2 cluster. Whereas in complex **1** the alkene and CO ligands adopt a staggered conformation relative to the vicinal CO ligands, in complex **5a** the bound alkene and the remaining ligands show an eclipsed conformation (Figure 2). Another important difference between **1** and **5a** is the alkene–Co bond lengths: in complex **1** the bonds are 2.14 and 2.18 Å, whereas in complex **5a** they are 2.13 and 2.16 Å, indicating stronger bonding to the metal center. Finally, and most interestingly, the alkene moiety is parallel and close to the Co–C_{alkyne} bond, the position in which olefin insertion should occur: the bond distances are 2.13 Å (Co1–C11) and 2.92 Å (C10–C2). Again, these

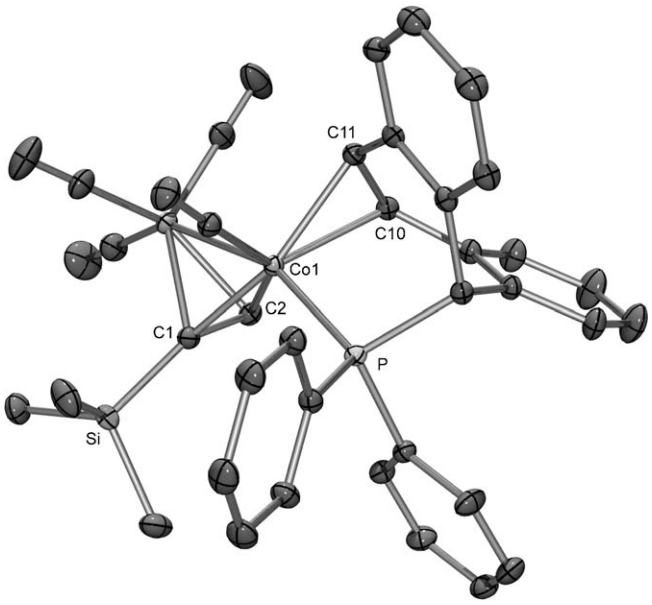


Figure 1. The crystal structure of complex **5a** (ORTEP diagram showing 50% probability ellipsoids).

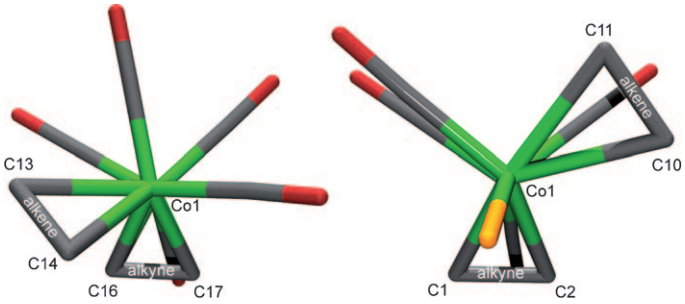
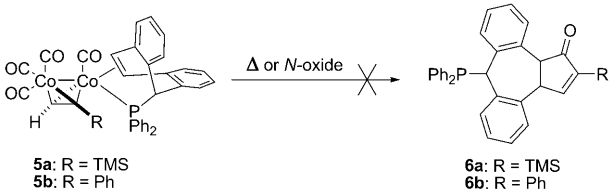


Figure 2. A comparison of the conformation of cobalt complexes **1** (staggered; shown on the left) and **5a** (eclipsed, shown on the right); red = oxygen, orange = phosphorus, grey = carbon, green = cobalt.

values contrast with those of **1**, in which the alkene is almost perpendicular to the Co[1]–C[16] bond (Figure 2).

The theoretical study of Milet, Gimbert et al.[6d] establishes that the insertion of ethene into the propyne dicobalt pentacarbonyl complex is favored if the olefin is in an axial coordination site, rather than an equatorial one; however, **5a** and **b** should readily overcome the energy barrier associated with reacting in the equatorial position (4.2 kcal mol^{-1} higher than the axial one). Moreover, rotation of the ML_3 vertex could bring the olefin into an axial coordination site. These authors also studied the insertion of several different olefins and concluded that the LUMO of the coordinated olefin is crucial to its reactivity in the PK reaction, as it determines the degree of backbonding that occurs, which is of paramount importance for C–C bond formation. Greater backbonding should facilitate the subsequent insertion. In terms of structure, the change in the C=C bond length in complexed versus uncomplexed olefins reflects the amount of backdonation from the filled d orbitals of Co into the empty π* orbitals of the olefin.[15] X-ray data reveal that the C=C bond length is 1.328 Å in **2** and 1.406 Å in **5a**, corresponding to a C=C bond lengthening of 0.077 Å.[16] This increase is greater than that calculated for norbornene (0.047 to 0.050 Å) and suggests that effective backbonding occurs between the metal and the alkene moiety in **5a**.

Despite the seemingly optimal geometry between the alkene and the Co–C bond, we were unable to identify any PK product. Both thermal activation (toluene, 110°C) and *N*-oxide activation (*N*-methylmorpholine *N*-oxide (NMO), CH_2Cl_2, RT) of complexes **5a** and **b** only resulted in decomposition products. However, the putative structures of the PK adducts corresponding to **5a** and **b** (**6a** and **b**, respectively, Scheme 4) are not strained. Furthermore, despite the

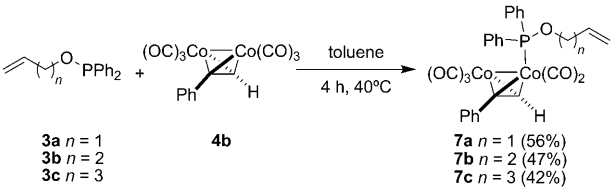


Scheme 4. Neither thermal nor *N*-oxide activation of complexes **5** yielded the desired Pauson–Khand products **6**.

equatorially positioned alkene, the geometries of the cobalt complexes seemed optimal. Thus, we attributed this lack of reactivity to two possible factors: the inherent inability of the dibenzo[*a,d*]cycloheptene system to undergo 1,2-insertion and the presence of a phosphine ligand at the same cobalt atom as the alkene (phosphine ligands are known to decrease the reactivity of alkyne–dicobalt carbonyl complexes[17]). To resolve this matter, we decided to study the phosphine–alkene ligands **3a–c**, which all feature a sterically unhindered, linear olefin.

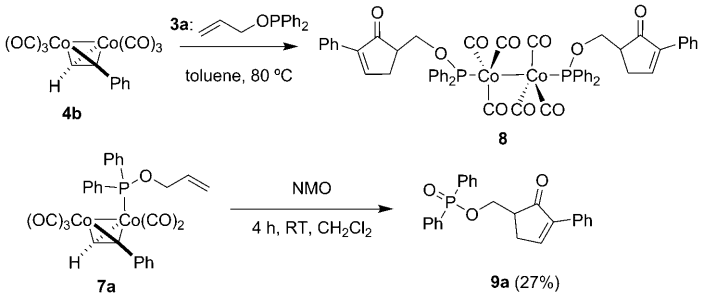
We prepared (prop-3-enyloxy)diphenyl phosphine (**3a**), (but-3-enyloxy)diphenyl phosphine (**3b**), and (pent-4-enyloxy)diphenyl phosphine (**3c**) by reacting the corresponding alkenyl alcohols with chlorodiphenyl phosphine. Reaction of phosphine–alkene ligands **3a–c** with phenylacetylene dicobalt complex **4b** at 40°C for 4 h afforded complexes **7a–c**, in which only the phosphine moiety is coordinated to the cobalt atom (Scheme 5).

Despite our efforts, we could not detect any complexes in which the alkene was coordinated to the cobalt atom. In one attempt, the reaction of phosphine **3a** with phenylacety-



Scheme 5. The reaction of phosphine–alkene ligands **3a–c** with phenylacetylene–hexacarbonyldicobalt.

lene–hexacarbonyldicobalt at 80 °C generated a novel red complex (**8**), which, despite being unstable in solution, was isolated by chromatography. X-ray, ^{1}H NMR, and IR data were consistent with **8** being a bisphosphine–hexacarbonyldicobalt complex in which the phosphines contained the PK adduct.[18] The IR spectrum of **8** shows a strong band at 1952 cm^{-1}, which is in full agreement with literature reports for similar complexes.[19] Complex **8** is likely to be formed, after the PK reaction, by rearrangement of the phosphine groups into a more stable cobalt complex (Scheme 6).



Scheme 6. The reactions of phosphine–alkene ligands with dicobalt–alkyne complexes.

To locate the PK adducts, we treated complexes **7a**–**c** with NMO at room temperature. Gratifyingly, complex **7a**, which contains an allyloxyphosphine group, provided the corresponding PK adduct **9a** in 27% yield (Scheme 6). The structure of **9a** was unambiguously assigned by X-ray crystallography (Figure 3). As expected, under *N*-oxide conditions the phosphinite group was oxidized to the corresponding phosphinate.

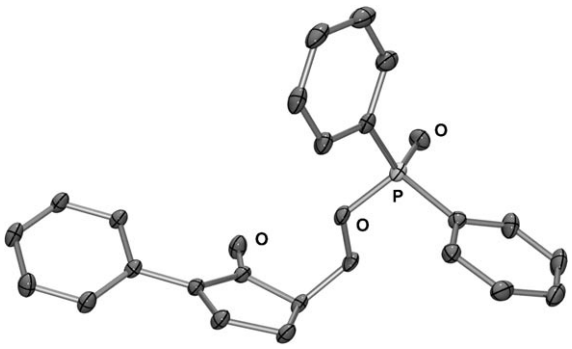


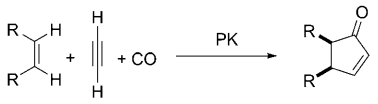
Figure 3. The crystal structure of **9a** (ORTEP diagram showing 50% probability ellipsoids).

Interestingly, if complexes **7b** and **c** were treated with NMO, under the same conditions as complex **7a**, or heated at 80 °C, only the starting materials were recovered. This indicates that the PK reaction occurs intramolecularly and that the length of the tether between the phosphorus group and the alkene is crucial to the olefin coordination and subsequent 1,2-insertion. This finding agrees with those of Krafft et al. for sulfide-directed PK reactions.[20]

The formation of compound **9a** confirms that, in contrast to the case of complexes **5a** and **b**, the alkene in **7a** coordinates to cobalt and readily undergoes 1,2-insertion to give the corresponding PK adduct. This reaction also indicates that the failure of the suberene system to undergo 1,2-insertion in complexes **5a** and **b** is not due to the coordination of a phosphorous atom, but to the olefinic system itself.[21]

Despite this progress, we were still perplexed as to why compounds **5** would not give the PK products despite being coordinated to cobalt and well positioned for olefin insertion. Although there is a general consensus that the best PK substrates are strained alkenes, there are some exceptions: for instance, ethene is a reasonably good substrate for intermolecular PK reactions,[22] yet is not strained. Thus, in trying to understand the reactivity of different olefins in PK chemistry, other features (e.g., substitution patterns) must also be considered. In this respect, we reasoned that the thermodynamics of the overall PK reaction could provide a rough estimate of the efficiency with which the energy contained in the original double bond is released during the formation of the cobaltacycle and that it should mimic the experimental reactivity observed for different alkenes.[23] To test this hypothesis, we calculated the energy release at the DFT level in PK reactions of acetylene with different olefins (Table 1).[24]

Table 1. Calculated energy release in PK reactions of acetylene with various olefins.



Alkene	ΔE [kcal mol^{-1}][a]	ΔE_{rel} [kcal mol^{-1}][b]
norbornene	−73.45	0.0
[2,2]paracyclophane-1,9-diene	−70.62	2.8
ethene	−69.86	3.6
cycloheptene	−67.50	5.9
cyclopentene	−65.37	8.1
cyclohexene	−61.52	11.9
(*Z*)-stilbene	−58.34	15.1
suberene	−52.67	20.8

[a] Reaction energies were calculated at the DFT level (B3LYP/6-31G*) and include zero-point energy corrections. [b] $\Delta E_{rel} = \Delta E$-(alkene)−$\Delta E$(norbornene).

As expected, norbornene—a reactive, strained alkene—leads to the most exoergic cyclization. Thus, we classified the olefins according to the endoergicity of their corresponding reactions relative to that of norbornene; thus, the values are expressed as ΔE_{rel}. We were pleased to observe that the calculated energies accurately parallel the observed experimental reactivities. Ethene is among the most reactive olefins in the PK reaction, with $\Delta E_{rel} = 3.8$ kcal mol^{-1} relative to norbornene. We anticipated unusual reactivity of the cyclic olefins—the calculated ΔE_{rel} for cycloheptene

(5.9 kcal mol^{-1}) indicates than it is more reactive than cyclopentene (8.1 kcal mol^{-1}) and cyclohexene (11.9 kcal mol^{-1}).[25] As a control experiment, we also calculated the energy of a single PK reaction of [2,2]paracyclophane-1,9-diene. De Meijere et al. have shown that [2,2]paracyclophane-1,9-diene, which is structurally related to suberene (they are both (*Z*)-1,2-diarylalkenes), undergoes rapid cyclization.[26] By thermodynamic analysis, we accurately predicted that the cyclophane alkene ranks among the most active alkenes for PK chemistry (Table 1). Gratifyingly, suberene was the least reactive of all the alkenes that we studied (ΔE_{rel} = 20.8 kcal mol^{-1}). This is in complete accordance with our experimental results and is consistent with the fact that complexes **5a** and **b** do not undergo the PK reaction. We believe that this lack of reactivity probably stems from the energy penalty associated to the loss of conjugation between the two benzene rings that would occur upon olefin insertion.[27]

Conclusion

In summary, we have prepared, isolated, and characterized (by X-ray crystallography) a new alkyne–tetracarbonyldicobalt complex (**5a**) containing a chelated phosphine–alkene ligand (**2**), in which the phosphorus atom and the alkene from the ligand are both attached to the same cobalt atom. Complex **5a** serves as a mechanistic model for an intermediate in the PK reaction. Although the alkene fragment is located in an equatorial coordination site with an appropriate orientation and, therefore, should undergo insertion, it failed to give the PK product upon either thermal or NMO activation. Conversely, phosphine–alkene **3a**, which contains a terminal alkene, readily provided the corresponding PK product. We attribute this reactivity to the differing ability of each olefin to undergo 1,2-insertion. Although terminal alkenes insert rapidly, the suberene moiety is not amenable to insertion, because this transformation involves the unfavorable loss of conjugation between the two benzene rings. These results underscore the premise that alkene coordination alone is not sufficient to enable alkene insertion in PK chemistry. Our experimental results, in good agreement with the theoretical calculations[5] and kinetic data,[16a] support the fact that the rate-determining step in the PK reaction is the alkene insertion.

We believe that phosphine–alkene ligands, in light of their utility in this study, should continue to prove invaluable in gaining further insight into the mechanism of the PK reaction.

Experimental Section

Dibenzo[*a,d*]cyclohepten-5-yldiphenyl phosphine borane complex (2-BH$_3$): Phosphine **2-BH$_3$** was prepared following a slightly modified literature procedure.[13a] Thionyl chloride (0.52 mL, 7.20 mmol) was added dropwise to a solution of dibenzosuberenol (500 mg, 2.40 mmol) in toluene (5 mL), at −15 °C. The solution was allowed to warm to room temperature and stirred overnight. The excess thionyl chloride and the solvent were evaporated under vacuum. The residue was dissolved in toluene and concentrated again to remove further excess thionyl chloride. This process was performed twice. The corresponding cycloheptenyl chloride was obtained as a purple solid and used in the next reaction without further purification.

A solution of Ph_2PH (0.46 mL, 2.64 mmol) in toluene (4 mL) was added to a solution of dibenzo[*a,d*]cyclohepten-5-yl chloride (544 mg, 2.40 mmol) in toluene (4 mL) and the mixture was heated at reflux overnight. The reaction was then cooled to room temperature and borane dimethylsulfide (0.29 mL, 3.12 mmol) was added. The reaction was stirred for 2 h at room temperature and quenched with water. After workup by extraction (EtOAc/water) the mixture was purified by silica gel column chromatography (1:1, hexane/EtOAc) and **2-BH$_3$** was obtained as a white solid (422 mg, 45 %). M.p. 187–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.05 (d, J = 14 Hz, 1H), 6.33 (s, 2H), 7.10–7.18 (m, 4H), 7.21–7.25 (m, 4H), 7.28 (dd, J = 7, 2 Hz, 4H), 7.38–7.50 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3 (d, J_P = 24 Hz, CH), 127.7 (d, J_P = 2 Hz, 2CH), 128.2 (d, J_P = 10 Hz, 4CH), 128.8 (d, J_P = 1 Hz, 2CH), 129.2 (d, J_P = 50 Hz, 2C), 129.9 (d, J_P = 2 Hz, 2CH), 131.0 (d, J_P = 2 Hz, 2CH), 131.2 (d, J_P = 5 Hz, 2CH), 132.0 (br s, 2CH), 133.8 (d, J_P = 8 Hz, 4CH), 134.1 (d, J_P = 1 Hz, 2C), 136.1 ppm (d, J_P = 4 Hz, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.9 ppm (br s); IR (film): $\tilde{\nu}_{max}$ = 1062, 1433, 2387 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{23}BP$ [*M*−H]$^-$: 389.1630; found: 389.1637.

[Co$_2$(μ-TMSC$_2$H)(CO)$_4$(C$_{27}$H$_{21}$P)] (5a): DABCO (39 mg, 0.35 mmol) and **4a** (97 mg, 0.25 mmol) were added to a solution of **2-BH$_3$** (90 mg, 0.23 mmol) in toluene (2 mL). The reaction was heated at 70 °C for 2 h. Then the solvent was evaporated and the mixture purified by silica gel column chromatography (30:1, hexane/EtOAc) to give **5a** as a red solid (70 mg, 42 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.05 (s, 9H), 4.53 (d, J = 15 Hz, 1H), 5.34–5.41 (m, 2H), 6.26 (d, J = 8 Hz, 1H), 6.66–6.80 (m, 6H), 6.86–6.98 (m, 8H), 7.25–7.28 (m,3H), 7.39 ppm (dd, J = 8.1 Hz, 1H); ^{13}C-{^{31}P} NMR (75 MHz, C_6D_6): δ = 1.3 (3CH$_3$), 53.9 (CH), 69.7 (CH), 77.6 (CH), 94.7 (CH), 126.3 (CH), 126.4 (CH), 127.2 (CH), 127.3 (CH), 127.6 (2CH), 127.9 (2CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 129.9 (2CH), 131.5 (C), 131.9 (C), 133.0 (2CH), 133.6 (2CH), 133.9 (C), 134.2 (C), 138.3 (C), 138.4 ppm (C) (one carbon signal is missing); ^{31}P NMR (121 MHz, C_6D_6): δ = 84.9 ppm (s); IR (film): $\tilde{\nu}_{max}$ = 2037, 1985 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{34}H_{32}Co_2O_2PSi$ [*M*+H−2CO]$^+$: 649.0573; found: 649.0585.

[Co$_2$(μ-PhC$_2$H)(CO)$_5$(C$_{15}$H$_{15}$OP)] (7a): A solution of **3a** (300 mg, 1.24 mmol) and **4b** (528 mg, 1.36 mmol) in toluene (8 mL) was heated at 40 °C for 4 h. Then the solvent was evaporated and the mixture purified by silica gel column chromatography (30:1, hexane/EtOAc) to give **7a** as a red oil (420 mg, 56 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 3.79–3.83 (m, 1H), 3.86–3.92 (m, 1H), 4.85 (d, J = 10 Hz, 1H), 5.00 (d, J = 17 Hz, 1H), 5.33 (d, J = 3 Hz, 1H), 5.39–5.46 (m, 1H), 6.88–6.94 (m, 9H), 7.33 (d, J = 6 Hz, 2H), 7.36–7.43 ppm (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ = 66.6 (d, J_P = 1 Hz, CH_2), 70.9 (s, CH), 86.7 (s, C), 116.6 (s, CH_2), 126.9 (s, CH), 128.1 (s, CH), 128.2 (d, J_P = 2 Hz, 2CH), 128.3 (d, J_P = 2 Hz, 2CH), 128.4 (s, 2CH), 130.4 (d, J_P = 12 Hz, 2CH), 130.6 (s, CH), 130.8 (s, 2CH), 130.9 (d, J_P = 13 Hz, 2CH), 133.2 (d, J_P = 9 Hz, CH), 137.3 (d, J_P = 42 Hz, C), 138.0 (d, J_P = 45 Hz, C), 138.5 ppm (s, C); ^{31}P NMR (121 MHz, C_6D_6): δ = 154.6 ppm (s); IR (film): $\tilde{\nu}_{max}$ = 1962, 2006, 2061 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{22}O_3Co_2P$ [*M*+H−3CO]$^+$: 518.9971; found: 518.9979.

(2-Oxo-3-phenylcyclopent-3-enyl)methyldiphenyl phosphinate (9a): A solution of NMO (237 mg, 1.03 mmol) in CH_2Cl_2 (4 mL) was added to a solution of **7a** (244 mg, 0.41 mmol) in CH_2Cl_2 (4 mL). The reaction was stirred at room temperature for 3.5 h. Then the solvent was evaporated and the mixture purified by silica gel column chromatography (2:1, hexane/EtOAc) to give **9a** as a white solid with some traces of cobalt (43 mg, 27 %). M.p. 136–137 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 2.05 (ddd, J = 10, 6, 2 Hz, 1H), 2.15–2.19 (m, 1H), 2.52 (dt, J = 19, 2 Hz, 1H), 4.15–4.25 (m, 2H), 6.87–6.94 (m, 4H), 6.99 (t, J = 3 Hz, 1H), 7.00–7.05 (m, 4H), 7.77–7.83 (m, 5H), 7.90–7.96 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.6 (s, CH_2), 47.2 (s, CH), 64.2 (s, CH_2), 127.2 (s, 2CH),

128.7 (s, 2CH), 128.8 (s, CH), 128.8–129.0 (m, $5C_{Ar}$), 131.6 (s, C), 131.7–132.5 (m, $7C_{Ar}$), 143.4 (s, C), 159.1 (s, CH), 206.0 ppm (s, C); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 30.9$ ppm (s); IR (film): $\tilde{\nu}_{max} = 1130$, 1228, 1438, 1700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{22}O_3P$ $[M+H]^+$: 389.1307; found: 389.1313.

Dimer 8: A solution of **3a** (400 mg, 1.65 mmol) and **4b** (640 mg, 1.65 mmol) in toluene (10 mL) was heated at 80 °C for 4 h. Then the solvent was evaporated and the mixture purified by silica gel column chromatography (2:1, hexane/EtOAc) to give **8** as a red solid (150 mg, 8%). Dimer **8** is rather unstable in solution and both the free PK adduct and dimer **8**, are observed by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.06$–2.20 (m, 2H), 2.49–2.57 (m, 1H), 4.17–4.37 (m, 2H), 6.82–6.95 (m, 3H), 7.00–7.22 (m, 7H), 7.68–7.96 ppm (m, 5H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 30.6$ (s, CH_2, dimer+PK adduct), 47.3 (t, $J_P = 4$ Hz, CH, dimer), 47.5 (d, $J_P = 7$ Hz, CH, PK adduct), 64.5 (d, $J_P = 6$ Hz, CH_2, dimer), 66.5 (s, CH_2, PK adduct), 126.0–144.4 (m, dimer+PK adduct), 158.1 (s, CH, dimer), 158.6 (s, CH, PK adduct), 202.9 (t, $J_P = 10$ Hz, $[Co(CO)_3]$, dimer), 205.3 (s, CO, dimer), 205.5 ppm (s, CO, PK adduct); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 30$ (s, PK adduct), 167 ppm (s, dimer); IR (film): $\tilde{\nu}_{max} = 1436$, 1703, 1952 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{22}O_3P$ [PK adduct+H]$^+$: 389.1307; found: 389.1313.

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