Tri- and Tetranuclear Homo- and Heterometallic Clusters as Precatalysts for the Pauson−Khand Reaction

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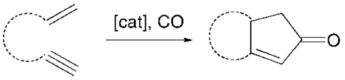
Tri- and tetranuclear clusters of formula C[$RuCo_3(CO)_{12}$] (C = NEt_4, **NEt_4-3**; C = bmim, **bmim-3**; C = H, **H-3**), [$Co_4(CO)_{12}$] (**4**), [$Co_4(CO)_{10}(\mu$-dppm)] (dppm = $Ph_2PCH_2PPh_2$) (**5**), [$Co_4(CO)_8(\mu$-dppa$)_2$] (dppa = $Ph_2PNHPPh_2$) (**6**), [$HFeCo_3(CO)_{11}(PPh_3)$] (**7**), and [(PNP)$PtCo_2(CO)_7$] (PNP = dppa, **8-H**; PNP = $C_6H_{13}SCH_2CH_2N(PPh_2)_2$, **8-S**; PNP = $PhN(PPh_2)_2$, **8-Ph**) were used as precatalysts in the intramolecular Pauson−Khand reaction of diethyl (allylpropargyl)malonate (**1**) under 8 bar of CO at 70 °C, which afforded the cyclopentenone **2**. The best results with 2% precatalyst loading were obtained with **NEt_4-3** and **bmim-3**, which gave isolated yields of 93 and 94%, respectively. With a 10% loading, **H-3** afforded a yield of 98%. Whereas the diphosphane-substituted Co_4 clusters **5** and **6** were inactive, the $PtCo_2$ clusters **8** (at 5% loading) afforded yields ranging from 85 to 91%. The enyne-substituted clusters **9** with a butterfly $RuCo_3$ metal core were isolated from the reaction of **NEt_4-3** with **1** and were characterized by ESI-MS and spectroscopic methods.

Introduction

The Pauson-Khand reaction (PKR) is formally a [2+2+1] cycloaddition of an alkyne, an olefin, and carbon monoxide, which yields a cyclopentenone derivative (Scheme 1).[1]

Scheme 1. The Pauson−Khand Reaction



This reaction was disclosed for the first time by Pauson and co-workers in the 1970s[2] and was typically performed using stoichiometric amounts of [$Co_2(CO)_8$] and the alkyne to form a dicobalthexacarbonyl−alkyne complex, which was subsequently reacted with an alkene. The first truly catalytic version of this reaction was reported in 1990 by Rautenstrauch,[3] and since then, several metal complexes of Rh, Ir, Ru, W, Ti, Mo, and Fe have been employed successfully. Efficient catalytic systems employed in the PKR include also cobalt-based heterodimetallic complexes[4] and nanoparticles.[5] The catalytic PKR is tolerant to a large variety of substrates and functional groups. In 1981, Schore[6] expanded the synthetic utility of the reaction and performed the first intramolecular PKR by connecting the alkene and alkyne moieties via a carbon linker. The PKR can also be performed asymmetrically when suitable chiral auxiliaries, complexes, or substrates are employed.[1,7] Although many variants of the PKR have expanded its scope and utility, the reaction mechanism continues to attract much attention. The generally accepted mechanism has been proposed by Magnus and Principe in 1985[8] for the [$Co_2(CO)_8$]-mediated PKR and takes into account the regio- and stereochemical outcomes of the reaction (Scheme 2).

The issue of the reaction mechanism has been addressed in several theoretical[9] and experimental[10] studies, which indicate that the loss of one CO ligand from a [alkyne-$Co_2(CO)_6$] complex (the second step in Scheme 2) precedes the olefin coordination−insertion and represents the rate-determining step of the process. In this context, it is noteworthy that a structurally characterized η^2-alkene-pentacarbonyldicobalt-alkyne complex has been recently reported.[11]

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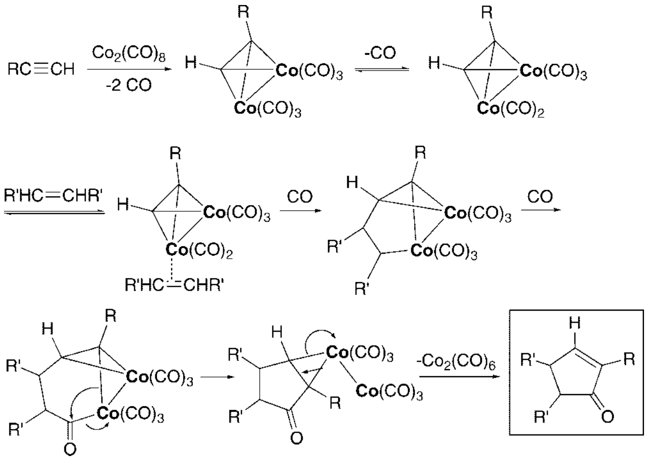
10.1021/om7010112 CCC: $40.75

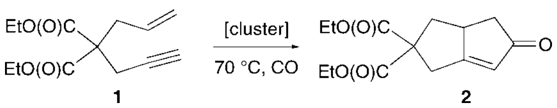
Scheme 2. The Accepted Mechanism for the PKR



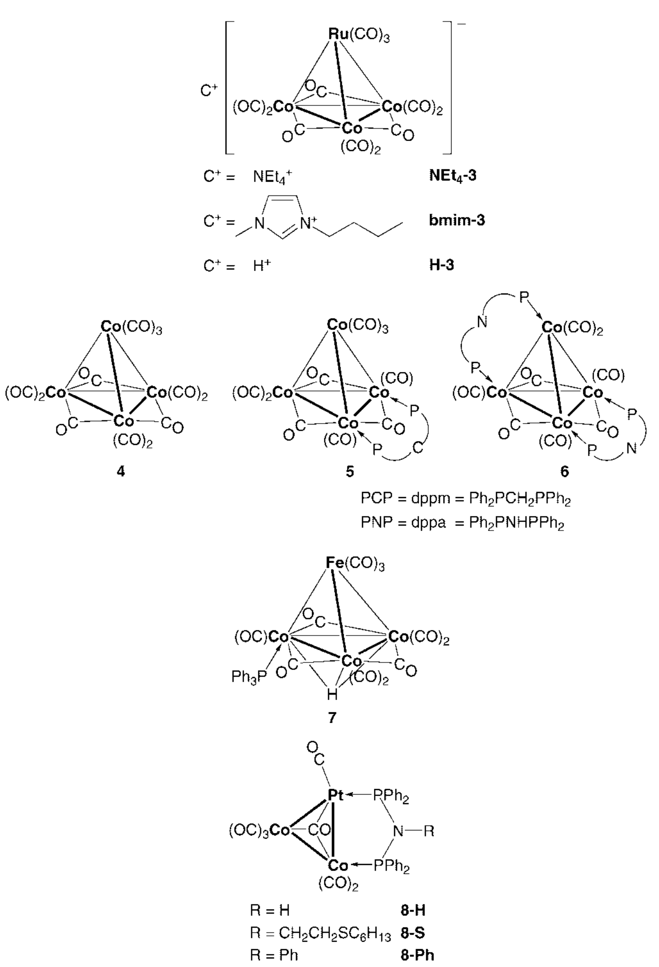
The PKR is a powerful tool for the one-pot synthesis of complex molecules containing the cyclopentenone functionality starting from simple components, and its high regio- and stereochemical control has resulted in extensive use in the synthesis of natural products and drugs.[1c,12]

Transition metal clusters are ideal molecules to study the synergistic effects brought about by the close proximity of metal centers and, in the case of heterometallic clusters, by their different chemical nature. This may lead to more efficient processes or to new types of reactions, stoichiometric or catalytic, while a fine-tuning of their performances, in terms of activity and selectivity, may be achieved by the choice of appropriate ligands.[13–15] Despite the increasing number of studies dealing with the use of clusters in homogeneous catalysis, the reported examples of cluster-catalyzed PKR are limited to the use of $[Co_4(CO)_{12}]$,[16] $[Co_3(CO)_9(\mu_3\text{-CR})]$,[17] or $[Ru_3(CO)_{12}]$.[18] In particular, Chung et al.[16a] reported a 92% yield for a reaction performed for 24 h at 150 °C under 10 atm of CO for diethyl (allylpropargyl)malonate using 1 mol % of $[Co_4(CO)_{12}]$, while Krafft et al.[16b] obtained a 94% yield after 13–18 h reaction time at 70 °C and 1 atm of CO for 4-dicarbethoxydec-1-en-6-yne with 5–10 mol % of $[Co_4(CO)_{12}]$ and $CyNH_2$ as promoter.

Scheme 3. The Model PKR



Scheme 4. Clusters Used as Precatalysts



As part of our studies on transition metal catalyzed C−C bond forming reactions,[19] including the PKR,[20] for which a model is shown in Scheme 3, we report here the first use of mixed-metal MCo_n carbonyl clusters (M = Fe, Ru, Co, n =

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Table 1. Effect of CO Pressure and Screening of Solvents[a]

entry	solvent	P_{CO} (bar)	time (h)[b]	yield (%)[c]
1	THF	1	9	60
2	THF	4	6	89
3	THF	8	3	92
4	THF	15	4	84
5	DME	8	5	72
6	dioxane	8	5	77
7	(bmim)BF_4	8	9	83

[a] Conditions: solvent 2 mL; temp 70 °C; substrate 0.50 mmol; catalyst 0.05 mmol of **NEt$_4$-3**. DME = 1,2-dimethoxyethane; bmim = 1-butyl-3-methylimidazolium. [b] Time to reach quantitative conversion. [c] Isolated yield of **2**.

Table 2. Catalysis with MCo_3 Clusters[a]

entry	metal core	cluster	loading (mol %)	time (h)[b]	conv (%)	yield (%)[c]
1	$RuCo_3$	**NEt$_4$-3**	10	3	100	92
2	$RuCo_3$	**NEt$_4$-3**	2	15	100	93
3	$RuCo_3$	**bmim-3**	10	2	100	90
4	$RuCo_3$	**bmim-3**	2	15	100	94
5	$RuCo_3$	**H-3**	10	4	100	98
6	$RuCo_3$	**H-3**	2	15	100	68
7	Co_4	$[Co_4(CO)_{12}]$ (**4**)	2	18	95	86
8	Co_4	$[Co_4(CO)_{10}(\mu\text{-dppm})]$ (**5**)	2	24	5	traces
9	Co_4	$[Co_4(CO)_8(\mu\text{-dppa})_2]$ (**6**)	2	24	5	–
10	$FeCo_3$	$[HFeCo_3(CO)_{11}(PPh_3)]$ (**7**)	7	24	95	65

[a] Conditions: THF 2 mL; temp 70 °C; 8 bar CO; substrate 0.50 mmol. [b] Time to reach a plateau in the conversion. [c] Isolated yield of **2**.

3; M = Pt, $n = 2$, Scheme 4) as precatalysts in the PKR under mild conditions using diethyl (allylpropargyl)malonate (**1**) as a substrate (Scheme 3).

Results and Discussion

The 60-electron tetrahedral cluster $NEt_4[RuCo_3(CO)_{12}]$ (**NEt$_4$-3**) was chosen to perform an initial screening of solvents and CO pressure conditions. The catalytic runs were carried out with a 10 mol % (with respect to **1**) cluster loading.

The results reported in Table 1 show that THF was the best solvent tested. Temperature and CO pressure were optimized at 70 °C and 8 bar, respectively. Lower temperatures (50 °C) led to incomplete conversions, while a CO pressure higher than ambient was necessary to avoid untimely deactivation of the catalyst (entry 1).

The study was continued by testing at various catalytic loadings three $RuCo_3$ anionic clusters differing only in the nature of the cation. Table 2 shows that quantitative conversions and very good yields of **2** were achieved even with a 2% catalyst loading using **NEt$_4$-3** and **bmim-3** (entries 2 and 4, respectively). Interestingly, with the latter precatalysts the productivity (as mol product/mol catalyst·h) was the same as that exhibited with a 10% catalyst loading. In the case of **H-3**, competing reactions led to only 68% yield at 2% loading (entry 6). The different reactivity observed when going from noncoordinating cations such as NEt_4^+ or $bmim^+$ to H^+ may be due to the slightly acidic conditions in the latter case,[21] which may trigger undesired side reactions.

Table 3. Catalysis with $PtCo_2$ Clusters[a]

entry	cluster	time (h)[b]	yield (%)[c]
1	**8-H**	8	85
2	**8-S**	4	93
3	**8-Ph**	5	91

[a] Conditions: THF, 2 mL; temp 70 °C; 8 bar CO; substrate 0.50 mmol; cluster 0.025 mmol. [b] Time to reach quantitative conversion. [c] Isolated yield of **2**.

We then extended the study of catalyst precursors to other isoelectronic 60-electron tetrahedral clusters having a Co_4 or a $FeCo_3$ core (Scheme 4). A comparison of entries 7, 8, and 9 with 2 shows that the activity of $[Co_4(CO)_{12}]$ (**4**) is comparable to that of **NEt$_4$-3** and that the presence of a diphosphane in the coordination sphere of the Co_4 clusters inhibits catalysis.[22] Cluster $[HFeCo_3(CO)_{11}(PPh_3)]$ (**7**) gave only a 65% product yield (at almost quantitative conversion) after 24 h and 7% loading (entry 10), thus confirming the detrimental effect of the presence of an acidic proton in the precatalyst.

The detrimental effect of the phosphorus ligand on the catalysis was not unexpected,[23] and Jeong et al. have reported that the presence of PPh_3 in catalytic reactions performed with $[Co_2(CO)_8]$ on diethyl (allylpropargyl)malonate significantly hampered the precatalyst activity and gave lower yields of the desired product.[24] Moreover, Laschat et al. have explained the lack of reactivity observed in the PKR with $[Co_2(CO)_6(\mu\text{-dppm})]$ by the *pseudoequatorial*-bridged arrangement in the corresponding alkyne complexes $[Co_2(CO)_4(\mu\text{-}\eta^2\text{-RCCR}')(\mu\text{-dppm})]$, which are not able to react further with the alkene because (i) the decarbonylation step becomes slower as a result of increased back-bonding to the remaining CO ligands and (ii) of the larger steric hindrance around the basal CO ligands to be substituted by the alkene (*syn* to the larger susbstituent R on the C−C triple bond).[25a]

Our study was extended by testing the catalytic activity of three trinuclear $PtCo_2$ clusters containing substituted bis(diphenylphosphanyl)amine ligands[26] (Scheme 4, Table 3). A minimum 5% precatalyst loading was necessary in order to reach complete conversion, and the yields ranged from 85 to 93%. It is noteworthy that in these cases the presence of a diphosphane in the coordination sphere of the cluster did not hinder the catalysis. A rationale for this behavior may reside in the coordination mode exhibited by the PNP ligands in the $PtCo_2$ clusters. We have previously shown that, contrary to what happens with $Ph_2PNHPPh_2$ (dppa), which acts exclusively as a bridging ligand in $PtCo_2$ clusters,[26b] some N-substituted bis(diphenylphosphanyl)amines can act both as bridging and chelating ligands, with the two forms being in equilibrium (Scheme 5).[26a]

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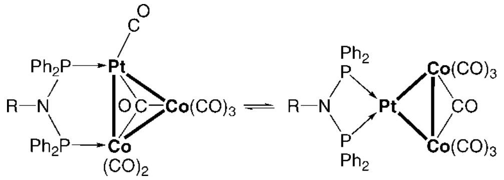
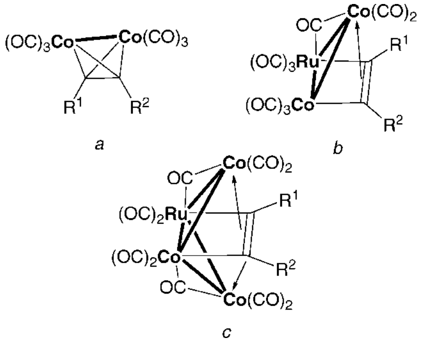
Scheme 5. Equilibrium between Bridged and Chelate Forms in (PNP)PtCo$_2$ Clusters



Scheme 6. Geometries of Alkyne-Substituted Clusters

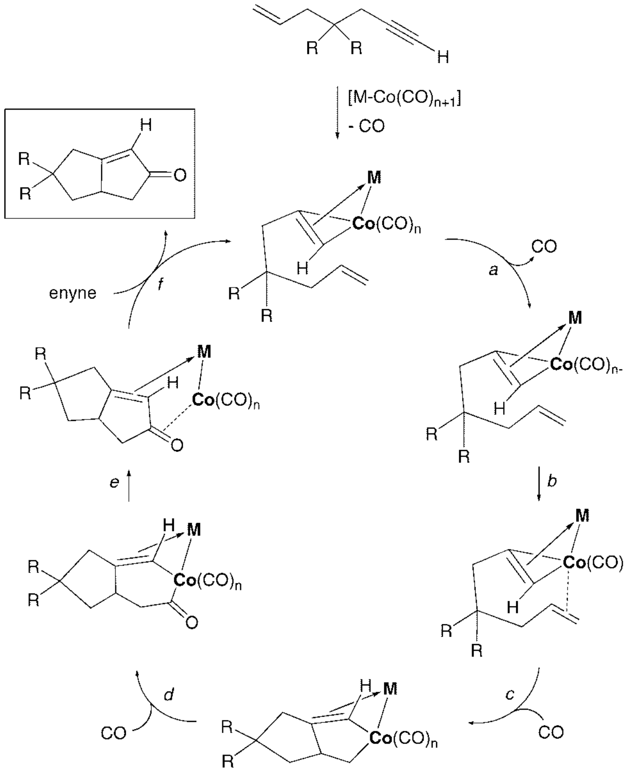


Given that in the PKR the dppa cluster **8-H** was less productive than **8-S** and **8-Ph**, it can be suggested that the presence of a P atom on at least one cobalt atom exerts the expected detrimental effect in the catalysis (*vide supra*). A similar effect of the coordination mode of the P ligand was observed with [Co$_2$(CO)$_6$(BINAP)] complexes, which were catalytically active when BINAP acted as chelating ligand,[27] but were inactive when BINAP exhibited a bridging behavior.[25a]

Mechanistic Considerations. The formation of the alkyne-substituted cluster (the first step of the reaction) is presumably accomplished by all the clusters used.[28] The different catalytic activities observed on going from dinuclear to tri- and tetranuclear clusters may thus be ascribed to the different ease with which the alkene moiety can interact with the Co atom bound to the ≡CH group. The solid-state structures reported in the literature for various alkyne-containing clusters present different possible orientations of the C−C ligand (Scheme 6).[29]

In the case of Co$_2$C$_2$ complexes where the C≡C bond is perpendicular to the Co−Co bond (type *a* in Scheme 6), the alkene can easily coordinate to form the cobaltacycle. Clusters of the type MCo$_2$C$_2$ (type *b*) have one face available for alkene coordination. In alkyne-MCo$_3$ clusters (type *c*), the C≡C bond is parallel to a M−Co bond and alkene coordination may become more difficult. In this case, however, the presence of *two* Co atoms available for alkene coordination might account for the satisfactory performance of MCo$_3$ clusters. On the other hand, in diphosphane-substituted clusters such as [Co$_4$(CO)$_8$(μ_4-η^2-RCCR)(μ-dppm)] or [Co$_4$(CO)$_6$(μ_4-η^2-RCCR)(μ-dppa)$_2$], some of the possible sites for alkene coordination are occupied by the phosphane ligand.

Scheme 7. General Mechanism for the Intramolecular PKR Catalyzed by Metal Clusters (M is a metal in the cluster not directly involved in the cobaltacycle formation)



Moreover, since only one cobalt atom is involved in the formation of the cobaltacycle, the other metals in the cluster (Ru, Fe, Pt, Co) may exert an electronic influence through metal−metal bonding, as suggested by Nakamura et al.[9b] On the basis of these considerations, a general catalytic cycle for the intramolecular PKR catalyzed by heterometallic clusters is depicted in Scheme 7, where “M” represents a metal in the cluster not directly involved in the cobaltacycle formation.

Formation of Enyne Adducts of NEt$_4$-3. When the reaction between **NEt$_4$-3** and **1** was carried out in refluxing THF in a 1:5 molar ratio, the enyne-cluster adducts **9a**,**b** could be isolated (Scheme 8).

The mixture of the two isomers of **9** is a deep violet thick oil showing in the ESI-HRMS(–) spectrum a signal at *m/z* 796.7709 Da with an isotopic pattern superimposable to that calculated for the formula [C$_{23}$H$_{18}$Co$_3$O$_{14}$Ru]$^-$ (Figure 1).

The IR spectrum of neat **9a**,**b** showed the presence of (i) ν(CO) absorptions at 2032, 1994, 1963 cm^{-1} (terminal) and 1816 cm^{-1} (bridging); (ii) ν(C(O)O) stretching at 1729 cm^{-1}; (iii) C(sp^2)H stretching at 3076 cm^{-1}; and (iv) a band of medium intensity at 1298 cm^{-1}, tentatively assigned to the CC stretching mode of the coordinated triple bond.[30] The ^{1}H NMR spectrum of **9a**,**b** in CD$_2$Cl$_2$ showed two broad singlets at δ 6.8 and 7.4,

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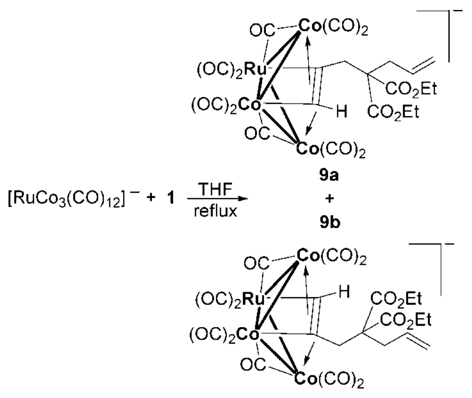
(27) (a) Gibson, S. E.; Lewis, S. E.; Loch, J. A.; Steed, J. W.; Tozer, M. J. *Organometallics* **2003**, *22*, 5382–5384. (b) Gibson, S. E.; Kaufmann, K. A. C.; Loch, J. A.; Steed, J. W.; White, A. J. P. *Chem.−Eur. J.* **2005**, *11*, 2566–2576.

(28) It is known that tetrahedral MCo$_3$ clusters (M = Co, Ru, Fe) and diphosphane-substituted Co$_4$ clusters react with alkynes to give butterfly Co$_4$C$_2$ complexes: (a) Choualeb, A.; Braunstein, P.; Rosé, J.; Welter, R. *Inorg. Chem.* **2004**, *43*, 57–71. (b) Braunstein, P.; Rosé, J.; Bars, O. *J. Organomet. Chem.* **1983**, *252*, C101–C105. (c) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612–1619. (d) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203–239. (e) Choualeb, A.; Rosé, J.; Braunstein, P.; Welter, R. *Organometallics* **2003**, *22*, 2688–2693. (f) Choualeb, A.; Braunstein, P.; Rosé, J.; Bouaoud, S.-E.; Welter, R. *Organometallics* **2003**, *22*, 4405–4417.

(29) See for example refs 28 for alkyne-Co$_4$ clusters and: (a) Aime, S.; Milone, L.; Osella, D.; Tiripicchio, A.; Manotti Lanfredi, A. M. *Inorg. Chem.* **1982**, *21*, 501–505. (b) Braunstein, P.; Rosé, J.; Bars, O. *J. Organomet. Chem.* **1983**, *252*, C101–C105. (c) Iwashita, Y.; Tamura, F.; Nakamura, A. *Inorg. Chem.* **1969**, *8*, 1179–1183. (d) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612–1619. (e) Sly, W. G. J. *Am. Chem. Soc.* **1959**, *81*, 18–20. (f) Baert, F.; Guelzim, A.; Poblet, J. M.; Wiest, R.; Demuynck, J.; Bénard, M. *Inorg. Chem.* **1986**, *25*, 1830–1841. (g) Dahl, C. F.; Smith, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 2450–2452. (h) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219–284, for other kinds of alkyne-containing clusters.

(30) Stanghellini, P. L.; Rossetti, R. *Inorg. Chem.* **1990**, *29*, 2047–2052.

Scheme 8. Formation of the Enyne-Substituted Clusters 9a,b



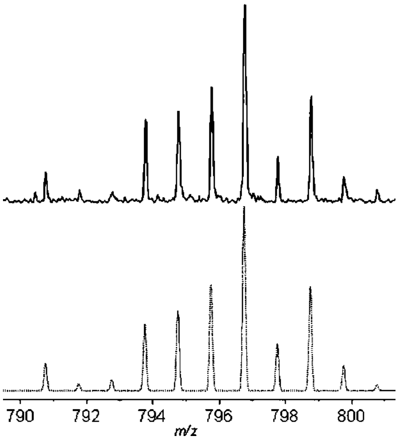


Figure 1. Experimental (top) and simulated (bottom) HRMS(−) spectrum of **9a**,**b** (exact mass of the anion $[C_{23}H_{18}Co_3O_{14}Ru]^-$ = 796.7736 Da) in $CDCl_3$, diluted with acetone. The error between simulated and observed isotopic patterns is 2.7 ppm.

which were assigned to the ≡CH moiety of the coordinated enyne of the two isomers.[28a] The $^{13}C\{^1H\}$ APT spectrum[31] did not show any signal ascribable to carbonyls, as expected for a fluxional system. Such fluxionality may also be responsible for the lack of signals unequivocally assignable to the coordinated acetylenic carbons.[32]

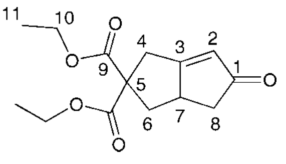
Conclusions

We have found that the Pauson−Khand reaction is efficiently catalyzed under mild conditions by tri- and tetranuclear clusters containing at least two Co atoms. Among the mixed-metal tetranuclear clusters tested, **bmim-3** and **NEt_4-3** gave the best results in terms of productivity and led to complete conversions of the substrate even at 2% catalyst loading. Clusters **5** and **6**, containing a diphosphane ligand, were almost inactive, while **7**, which contains a monodentate phosphane and an acidic proton, exhibited moderate activity. The effect of diphosphane ligands on catalytic activity was found to depend on the metal skeleton. With the $PtCo_2$ clusters **8**, the productivity was higher when ligand chelation on the Pt atom was favored, confirming that the presence of P ligands on Co atoms exerts a detrimental effect. The enyne-substituted clusters **9a**,**b** were isolated and their structures confirmed by HRMS and NMR analyses.

Experimental Section

All reactions and manipulations were carried out under argon for the synthesis of the clusters or under CO atmosphere for the catalytic experiments. Diethyl (allylpropargyl)malonate (**1**),[33] $NEt_4[RuCo_3(CO)_{12}]$, $[HRuCo_3(CO)_{12}]$,[21,34] $[Co_4(CO)_{10}(\mu\text{-dppm})]$,[28f] $[Co_4(CO)_8(\mu\text{-dppa})_2]$,[35] $[HFeCo_3(CO)_{11}(PPh_3)]$,[21] and $[(PNP)PtCo_2(CO)_7]$[26] were synthesized according to literature procedures and characterized by IR and multinuclear NMR spectroscopic methods. All the other reagents were commercially available and used as received. Solvents were HPLC grade and were dried and distilled under nitrogen before use.[36] Flash chromatography was performed on SiO_2 Kieselgel 230–400 mesh. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz for ^1H) at 295.0 K, chemical shifts are reported in ppm referenced to $SiMe_4$ for ^1H and ^{13}C and $K_3[Co(CN)_6]$ for ^{59}Co, and the ^1H and ^{13}C signals were assigned by means of $^{13}C\{^1H\}$APT, ^1H COSY, $^1H-^{13}C$ HMQC, and $^1H-^{13}C$ HMBC experiments. Deuterated solvents were purchased from Aldrich or Acros and stored under inert atmosphere of dinitrogen on molecular sieves. The IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. GLC analyses were performed on an HP5890 instrument equipped with a Supelco SPB-1 capillary column (30 m × 320 μm × 0.25 μm); GC-MS analyses were performed on an HP6890-HP5973MSD instrument equipped with an HP-5MS capillary column (30 m × 250 μm × 0.25 μm). The mass spectrometry analysis of **9** was performed using a time-of-flight mass spectrometer equipped with an electrospray ion source (Bruker microTOF) in negative ion mode. The sample solution ($CDCl_3$/acetone) was introduced by continuous infusion with the aid of a syringe pump at a flow rate of 180 mL/min. The mass spectrometric parameters were as follows: end plate offset −500 V, capillary −4500 V, capillary exit −80 V, skimmer1 −35 V, nebulizer pressure 0.4 bar, drying gas flow 5.0 L/min, and drying gas temperature 200 °C. The software used for the simulations is Bruker Daltonics DataAnalysis (version 3.3).

Synthesis of bmim-3. This cluster was synthesized according to the literature procedure[34] by replacing NEt_4Cl with 1-butyl-3-methylimidazolium chloride. IR (KBr): ν_{CO} = 1996 (vs), 1968 (vs), 1803 (vs) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.0 (3H, CH_3), 1.4 (2H, CH_2), 1.9 (2H, CH_2), 4.0 (3H, CH_3), 4.2 (2H, CH_2), 7.4 (2H, 2CH), 8.3 (1H, CH). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 13.0 (CH_3), 19.4 (CH_2), 31.8 (CH_2), 36.8 (CH_3), 50.5 (CH_2), 122.9 (CH), 124.1 (CH), 134.2 (C), 211.8 (br, CO). ^{59}Co NMR (95 MHz, CD_2Cl_2): δ −2631.



Catalytic Runs. In a typical catalytic run a 20 mL glass liner was charged with the cluster (0.010 mmol), enyne **1** (0.119 g, 0.50 mmol), and THF (2 mL) under CO atmosphere, the glass liner was then transferred to a stainless steel autoclave equipped with a digital manometer, and the autoclave was pressurized with CO and heated to 70 °C with stirring. After the reaction was complete, the solvent was evaporated under reduced pressure and the product **2** was purified by flash chromatography through silica gel (diethyl ether/*n*-hexane, 6:4) and characterized by GC-MS, IR, and ^1H and ^{13}C NMR. The reported isolated yields are the mean values for at least two runs; the yields of the replicates did not differ by more than

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[31] The spectrum was acquired at 295 K with 35856 scans, an acquisition time of 1.2 s, and a recycling delay of 5 s.

[32] Two signals at δ 125.4 and δ 130.7 can be tentatively assigned to the ≡CH carbons of the two isomers.

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[34] Braunstein, P.; Rosé, J. *Inorg. Synth.* **1989**, *26*, 356–359.

[35] Moreno, C.; Macazaga, M. J.; Marcos, M. L.; González-Velasco, J.; Delgado, S. *J. Organomet. Chem.* **1993**, *452*, 185–192.

[36] *Purification of Laboratory Chemicals*, 5th ed.; Armarego, W. L. F., Chai, C. L. L., Eds.; Butterworth-Heinemann, 2003.

5%. IR (neat): $\nu = 1729$ (vs, ν_{COO}), 1637 (vs, ν_{CO}) cm^{-1}. GC-MS (70 eV, EI): *m/z* (%): 266 [M^{+}] (52), 221 (26), 192 (68), 164 (33), 147 (7), 136 (12), 119 (100), 91 (69), 77 (11), 65 (15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.2 (6H, H^{11}), 1.7 (1H, H^{6}), 2.1 (1H, H^{8}), 2.6 (1H, H^{8}), 2.8 (1H, H^{6}), 3.1 (1H, H^{7}), 3.3 (2H, H^{4}), 4.2 (4H, H^{10}), 5.9 (1H, H^{2}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 13.9 (C^{11}), 35.1 (C^{4}), 38.8 (C^{6}), 42.0 (C^{8}), 45.0 (C^{7}), 60.8 (C^{5}), 62.0 (C^{10}), 62.1 (C^{10}), 125.4 (C^{2}), 170.7 (COO), 171.4 (COO), 186.1 (C^{3}), 210.0 (CO).

Synthesis of 9. To a solution of $NEt_4[RuCo_3(CO)_{12}]$ (0.122 g, 0.16 mmol) in THF (20 mL) was added the enyne **1** (0.190 g, 0.80 mmol). The solution was stirred overnight at reflux under argon atmosphere, and its color changed from dark red to dark violet. The resulting suspension was then filtered on a short Celite pad; the solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (5 × 10 mL) and dried under vacuum. IR (neat): 3076 (w), 2983 (s), 2964 (s), 2937 (s), 2909 (s), 2874 (s), 2032 (vs, ν_{CO}), 1994 (vs, ν_{CO}), 1963 (vs, ν_{CO}), 1816 (vs, ν_{CO}), 1729 (vs, ν_{COO}), 1640 (m), 1464 (s), 1447 (s), 1394 (s), 1367 (s), 1259 (vs), 1298 (m, ν_{C2Co2}), 1096 (m), 1066 (s), 923.0 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.2 (CH_3), 1.7–3.4, 4.2 (CH_2), 5.1 ($=CH_2$), 5.7 ($=CH$), 6.8 and 7.4 (coordinated $\equiv CH$ of the two isomers); all signals are broad. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 13.9 (CH_3), 61.4 (CH_2), 119.0 ($=CH_2$), 125.4 and 130.7 (coordinated $\equiv CH$), 132.9 ($=CH$), 170.6 (COO), 171.8 (COO).

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Supporting Information Available: IR and NMR spectra of **1**, **2**, **bmim-3**, and **9a-b** and HRMS spectrum of **9a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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