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On Early Events in the Pauson–Khand Reaction

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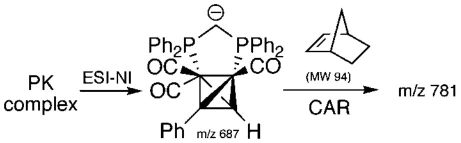
ABSTRACT

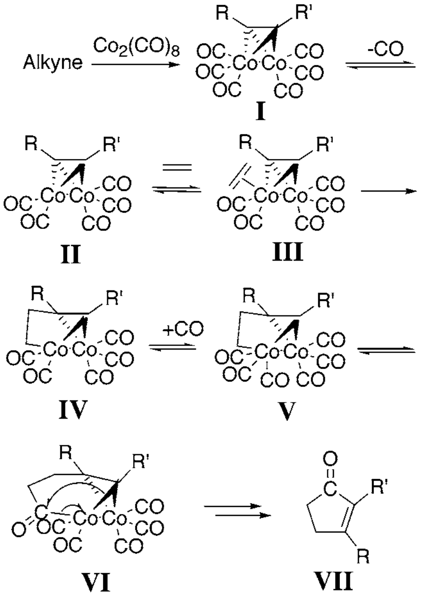


The Magnus Pauson–Khand (PK) mechanism has been studied for the first time by electrospray ionization coupled to tandem mass spectrometry. It has been found that loss of CO from the PK complex precedes olefin coordination and insertion.

The pathway suggested in 1985 by Magnus and co-workers[1] for the Pauson−Khand (PK) reaction,[2] a cobalt-mediated joining of an alkyne, an olefin, and carbon monoxide (Scheme 1), is widely accepted despite a dearth of evidence for the postulated intermediates.[3] We report in this Letter the observation by mass spectrometry of proposed key intermediates in this synthetically useful and mechanistically intriguing reaction.

In the pathway advanced by Magnus and co-workers, the stable and fully characterized[4] alkyne−$Co_2(CO)_6$ complex **I** initially suffers loss of a CO ligand from one of the two Co atoms (complex **II**), which is followed by olefin coordination (complex **III**) and insertion (complex **IV**). However, ex-

Scheme 1. Postulated Mechanism of the Pauson−Khand Reaction



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(2) For reviews, see: (a) Schore, N. E. *Org. React.* **1991**, *40*, 1−90. (b) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341. (c) Brummond, K. M.; Kent, J. L *Tetrahedron* **2000**, *56*, 3263−3283. (d) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc. Perkin Trans. 1* **2000**, 1657−1668.

(3) Complex **II** (Scheme 1), generated photochemically, has been identified by IR spectroscopy. See: (a) Gordon, G. M.; Kiszka, M.; Dunkin, I. R.; Kerr, W. J.; Scott, J. S.; Gebicki, J. *J. Organomet. Chem.* **1988**, *554*, 147−154. (b) Draper, S. M.; Long, C.; Myers, B. M. *J. Organomet. Chem.* **1999**, *558*, 195−199. For ligand stabilization of **II**, see: (c) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199−7207. (d) Verdaguer, X.; Moyano, A.; Pericas, M. A.; Riera, A.; Bernardes, V.; Greene, A. E.; Alvarez-Larena, A.; Piniella, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 2153-2154.

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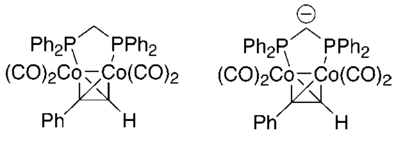
perimental evidence for these key mechanistic components has been lacking: complex **I**, on heating in the presence of an olefin, is converted into the final product **VII** without isolable or even, to date, detectable intermediates.[3] Recent quantum mechanical studies[5] of the Magnus PK reaction pathway appear to preclude the possibility of actually isolating any of the intermediates and, in fact, indicate that mere observation of the different species could be difficult at best. The most energetically demanding step in the PK process turns out to be the loss of CO from complex **I** to generate complex **II** (26.4 kcal/mol above complex **I**, acetylene as the alkyne). The transition state (14.4 kcal/mol activation energy) involved in the conversion of complex **III** (11.8 kcal/mol under **II**, ethylene as the alkene) into complex **IV** (1.1 kcal/mol above complex **III**), as well as all subsequent steps (insertion of CO, reductive elimination), is much less energetically demanding and thus the PK reaction, following formation of **II**, should indeed proceed rapidly to the final product, as is experimentally observed.

Electrospray ionization coupled to gas-phase reactive collision processes is particularly useful for studying stepwise events in the transformation of transition-metal compounds with intact or largely intact coordination spheres because of its high degree of tolerance of weakly bound ligands.[6] The liganded species of interest, ionized and naked in the gas phase, can be isolated and its evolution studied, without interference from other ionized or neutral compounds, by tandem mass spectrometry. To investigate the PK reaction mechanism through this means, the symmetrical bis(diphenylphosphino)methane (DPPM) adduct with phenylacetylene−dicobalt hexacarbonyl ($\mathbf{I}_{dppm}$, Figure 1), which was expected[7] to be well-suited for study by negative ion electrospray mass spectrometry, was prepared.[8]



$\mathbf{I}_{dppm}$

$[\mathbf{I}_{dppm}\text{ - H}]^-$

Figure 1. Structures of neutral $[\mathbf{I}_{dppm}]$ and ionized $[\mathbf{I}_{dppm}\text{-H}]^-$ DPPM−phenylacetylene−dicobalt tetracarbonyl complexes.

On the basis of the literature,[7] deprotonation of $\mathbf{I}_{dppm}$ under negative ion electrospray ionization conditions (see Experimental Parameters) was expected to occur at the methylene site to yield the ion at *m*/*z* 715 $[\mathbf{I}_{dppm}\text{-H}]^-$. This indeed was observed (base peak), together with a series of fragments at *m*/*z* 687 (32%), *m*/*z* 659 (28%), and *m*/*z* 631 (1.5%), which corresponded to $[(\mathbf{I}_{dppm}\text{-H})\text{-CO}]^-$, $[(\mathbf{I}_{dppm}\text{-H})\text{-2CO}]^-$, and $[(\mathbf{I}_{dppm}\text{-H})\text{-3CO}]^-$, respectively.[9] The parent $[\mathbf{I}_{dppm}\text{-H}]^-$ ion was then selected and submitted to low-energy reactive collisions ($E_{lab} = 4$ eV, with norbornene as the reactive target) in the collision cell for the purpose of ascertaining whether the fully coordinated complex was capable of olefin association. The expected collision-induced dissociation (CID) process, which involved consecutive CO loss from $[\mathbf{I}_{dppm}\text{-H}]^-$ (first two ions in relatively high abundance, third in relatively low abundance), and a collision-activated reaction (CAR) process that produced an adduct ion at *m*/*z* 781, but significantly not at *m*/*z* 809 $\{[(\mathbf{I}_{dppm}\text{-H}) + \text{norbornene}]^-$, *m*/*z* $[715 + 94]\}$, were observed. The complete absence of an adduct ion at *m*/*z* 809 argued strongly against the possibility that the ion at *m*/*z* 781 issued from that at *m*/*z* 809 by loss of CO and pointed to the alternative stepwise mode for the CO/norbornene ligand exchange (loss of CO, then addition of norbornene), or possibly a direct exchange, followed or not by insertion of the norbornene as proposed by Magnus and co-workers.

To determine whether a direct or indirect CO/norbornene ligand exchange was operating, the initially observed $[(\mathbf{I}_{dppm}\text{-H})\text{-CO}]^-$ (*m*/*z* 687) ion was selected and submitted to low-energy collisions with norbornene[10] under precisely the same collision conditions, which gave the CAR spectrum shown in Figure 2. The norbornene addition product ion at *m*/*z* 781 suggested that the $[(\mathbf{I}_{dppm}\text{-H})\text{-CO}]^-$ ion could indeed be the precursor of the norbornene adduct on starting from the $[\mathbf{I}_{dppm}\text{-H}]^-$ ion. This supposition was confirmed by the identical [*m*/*z* 687]/[*m*/*z* 781] ion abundance ratios that were

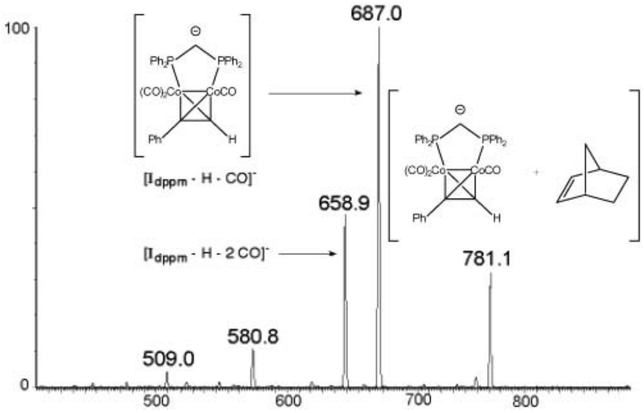


Figure 2. CAR spectrum of $[(\mathbf{I}_{dppm}\text{-H})\text{-CO}]^-$ *m*/*z* 687, with norbornene under ESI conditions.

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(4) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323−377.

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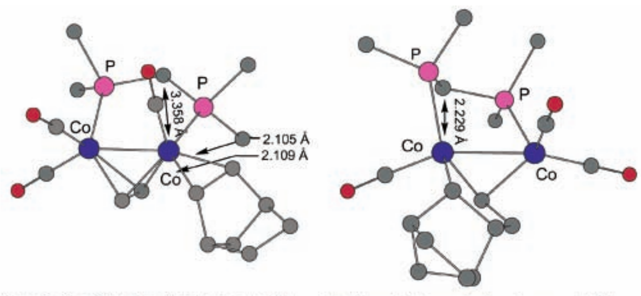
(9) The ion at *m*/*z* 751 (45%) was also observed and corresponded, according to the isotopic profile, to $(M + Cl)^-$.

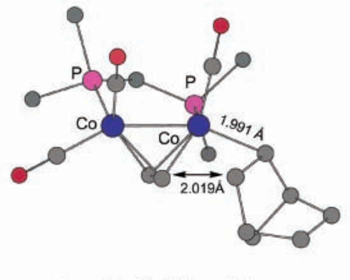
(10) That the presence of the unsaturation is necessary for the formation of an adduct with $[\mathbf{I}_{dppm}\text{-H-CO}]^-$ was demonstrated by using norbornane in the collision cell, which, as expected, did not produced an adduct ion at *m*/*z* 783.

found to have resulted from the CAR experiments with m/z 687 and m/z 715 as the precursor ions. *Formation of the adduct ion, thus, does not occur to any significant degree by a direct CO/norbornene ligand exchange in the [($\mathbf{I}_{dppm}$-H)]$^-$ ion, but takes place quasiexclusively through initial CO loss from this ion to give the [($\mathbf{I}_{dppm}$-H)-CO]$^-$ ion, which then forms the norbornene adduct.*

To discern whether the adduct ion at m/z 781 ion was the Magnus association complex analogous to **III** or the more advanced Magnus insertion cobaltacycle complex analogous to **IV**, the respective energies were evaluated[11] through density functional theory calculations (B3LYP/LANL2DZ* level) with Gaussian 98 (for expediency, the phenyls of dppm were replaced by methyls, and the phenyl in phenylacetylene by H). The structures are shown in Figure 3. The cobaltacycle complex was found to be 22 kcal/mol lower in energy than the association complex with an activation energy of 12 kcal/mol, which leads to the conclusion that the adduct ion at m/z 781 must be the more advanced complex.[12] The significant energy difference between the two complexes may reflect, in part, stabilization within the cobaltacycle of the Co with the free coordination site by the P-CH$^{(-)}$-P charge. The clear deformation of the dppm ligand in this complex would appear to support this supposition.



Association Complex (analogous to **III**) Cobaltacycle Complex (analogous to **IV**)



Transition State **III** ⟶ **IV**

Figure 3. Geometries for the two possible structures of the adduct ion at m/z 781 and TS (**III** → **IV**) (hydrogens omitted for clarity).

In conclusion, negative ion electrospray collision experiments and theoretical calculations together have permitted early events and their chronology to be defined in the gas-phase conversion of $\mathbf{I}_{\mathrm{dppm}}$: loss of carbon monoxide, olefin coordination, and olefin insertion. This elucidation, importantly, is in harmony with the theoretical results of Nakamura and co-workers,[5] who were unable to locate a low-energy transition state for the direct formation of an olefin-associated complex, which would have provided an alternative to the pathway initiated by loss of CO that is delineated above. Thus, for the first time, the widely accepted Magnus PK mechanism has solid support, albeit from gas-phase experiments.[13]

Acknowledgment. We thank Prof. P. Dumy for his interest in our work, the CECIC for providing computer facilities, and the CNRS for financial support.

Supporting Information Available: Cartesian coordinates of all the structures reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] For computational details, see: de Bruin, T. J. M.; Milet, A.; Robert, F.; Gimbert, Y.; Greene, A. E. *J. Am. Chem. Soc.* **2001**, *123*, 7184−7185.

[12] The possibility that the ion at m/z 781 is, in fact, the yet more advanced carbon monoxide insertion product analogous to **VI** (*but* with an additional vacant site on Co due to the absence of CO in the collision cell), formed directly from the cobaltacycle complex analogous to **IV**, seems improbable from energy considerations.

[13] **Experimental Parameters.** The negative ion electrospray mass spectra and the CID and CAR mass spectra, in low-energy collision range, were obtained with a modified triple-quadrupole Quattro 1 mass spectrometer (Micromass, Manchester, England). Samples were prepared in CH_3OH (50 ng/μLl) and were introduced into the electrospray source through a stainless steel capillary with a syringe pump. The solvent flow was fixed at 400 μL/h. The ESI source conditions were as follows: voltage offset between the needle and the counter electrode, 3.5 kV; cone voltage, −30V or −50 V.; source temperature, 100 °C.; drying gas (N_2) flow, 400 L/h; nebulizing gas flow, 15 L/h. The CID spectra of the selected precursor ions, using argon as the target gas in the collision cell, were obtained at a pressure of 10^{-4} mBar and with a collision energy of $E_{\mathrm{lab}} = 20$ V. The CAR experiments, using norbornene gas in the cell, were performed at a pressure of 2.5×10^{-3} mBar and with a laboratory collision energy of ca. 4 eV. To introduce vaporized norbornene into the collision cell, solid norbornene was placed in a glass flask that was connected to the collision cell of the tandem mass spectrometer by means of a micrometric valve and to a rotary pump to remove residual air. The use of lens voltages 7, 8, and 9 (350, 0, and 0 V, respectively) was crucial for successfully storing the selected precursor ions for the CAR experiments. (These lens voltages led to an improvement in the efficiency of anion production of up to 60-fold in comparison with the results obtained under standard CID conditions, which required a higher collision energy and a lower pressure of the inert gas target.)