Intramolecular Phosphine Attack on a Coordinated Alkyne Ligand in $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CH})$. Characterization of the Zwitterionic Hydrocarbyl Complex $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$

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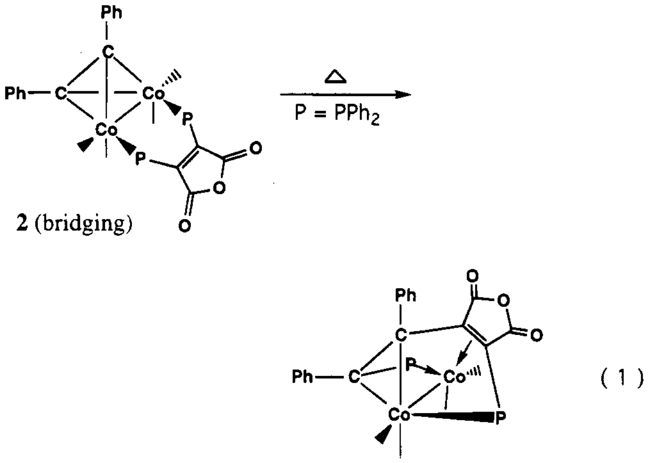
*Summary: The chelating diphosphine complex $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CH})$ (**1**) gives the zwitterionic hydrocarbyl-bridged compound $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ (**3**) in refluxing 1,2-dichloroethane. Binuclear **3** is formed by a regioselective attack of one of the PPh_2 moieties on the terminal alkyne carbon. The hydrocarbyl complex has been isolated and characterized in solution by IR and NMR spectroscopy. The solid-state structure of $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ has been determined by X-ray diffraction analysis, which confirms the identity of the eight-electron hydrocarbyl ligand in **3**. This work represents the first example of an intramolecular phosphine addition to a coordinated alkyne to give a μ-η^2:η^1-hydrocarbyl moiety.*

Examples of PR_3 attack on a transition-metal-coordinated alkyne ligand to afford a zwitterionic complex that contains a μ-η^2:η^1-hydrocarbyl moiety are exceedingly rare. The only known example involves the reaction between $CpRh(CO)(PMe_3)$ and $Os(CO)_4(\eta^2\text{-HC}{\equiv}\text{CH})$, which yields $CpRhOs(CO)_3(\mu\text{-CO})[\mu\text{-}\eta^2{:}\eta^1\text{-HCCH(PMe}_3)]$, presumably as a result of an intermolecular PMe_3 attack on the acetylene ligand.[1–3]

We have recently reported that thermolysis of $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CPh})$ (**2**, chelating isomer; bma = $(Ph_2P)\text{C=C(PPh}_2\text{)C(O)OC(O)}$) in 1,2-dichloroethane results in an initial isomerization to give the corresponding bma-bridged complex; this latter isomer then undergoes an alkyne–diphosphine ligand coupling and formation of $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}(Z)\text{-Ph}_2\text{PC(Ph)=(Ph)CC=C(PPh}_2\text{)C(O)OC(O)}]$ (eq 1).[4] However, while examining the reactivity of the corresponding phenylacetylene complex $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CH})$ (**1**), we observed a different course of reactivity in the thermolysis of **1**, involving the attack of a PPh_2 moiety on the terminal alkyne carbon to give the new complex $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ (**3**). Whereas the insertion chemistry of $Co_2(CO)_6(\mu\text{-alkyne})$[5] and the nucleophilic addition reactions to $[Co_2(CO)_6(\text{propargyl})]^+$ [6] are well-documented, the reactivity of the coordinated alkyne ligand with a coordinated diphosphine is without precedent.



2 (bridging)

(1)

During the course of our studies on the reactivity of $Co_2(CO)_6(\mu\text{-PhC}{\equiv}\text{CH})$ with the diphosphine ligand bma, we have prepared and isolated the bma-substituted complex $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CH})$ (**1**). Spectroscopic data indicate that the ancillary bma adopts a chelating mode in **1**. Our initial desire was to explore the reactivity of the coordinated bma and phenylacetylene ligands as part of our interest in the P–C cleavage chemistry exhibited by the bma ligand.[4,7] Refluxing a 1,2-dichloroethane solution of $Co_2(CO)_4(bma)(\mu\text{-PhC}{\equiv}\text{CH})$[8] (chelating isomer) leads to the formation of the zwitterionic hydrocarbyl complex $Co_2(CO)_4[\mu\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$, in an isolated yield of 70%.[9] When the reaction is monitored by ^{31}P NMR spectroscopy, the formation of the bridging bma-substituted complex of **1** (<2%) is observed (eq 2), and on the basis of the chemistry observed with the related

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[1] Takats, J.; Washington, J.; Santarsiero, B. D. *Organometallics* **1994**, *13*, 1078.

[2] For examples of phosphine addition to coordinated acetylide complexes, see: (a) Cherkas, A. W.; Doherty, S.; Cleroux, M.; Hogarth, G.; Randall, L. H.; Breckenridge, S. M.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 1701 and references therein. (b) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717 and references therein. (c) Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29.

[3] For a report on the attack of PMe_3 on mononuclear alkyne complexes, see: Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. *Organometallics* **1993**, *12*, 4312 and references therein.

[4] Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics*, in press.

[5] (a) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323. (b) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199. (c) Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley-Interscience: New York, 1990, Chapter 9.

[6] (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749.

[7] Yang, K.; Smith, J. M.; Bott, S. G.; Richmond, M. G. *Organometallics* **1993**, *12*, 4779.

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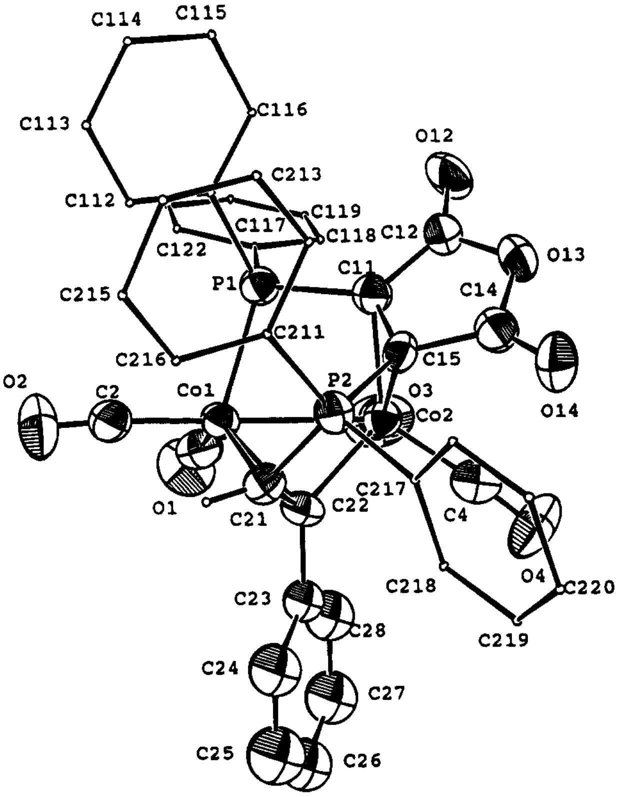
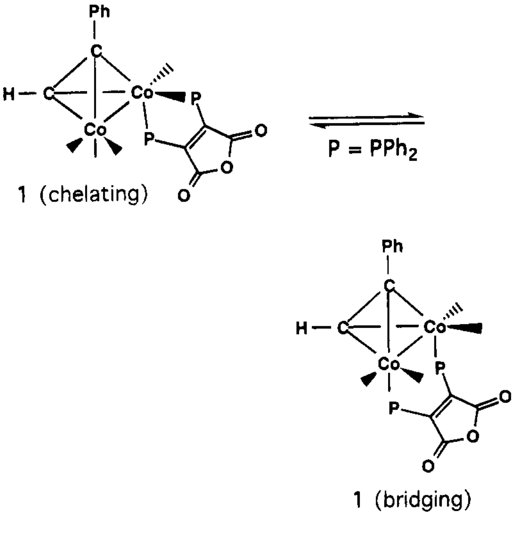


Figure 1. ORTEP drawing of **3**. Selected bond distances (Å) and angles (deg): Co(1)–Co(2) = 2.549(1), Co(1)–C(21) = 2.015(8), Co(1)–C(22) = 1.899(7), Co(2)–C(22) = 2.005(7), Co(1)–P(1) = 2.204(2), C(21)–P(2) = 1.758(7); Co(1)–C(21)–P(2) = 111.4(4), Co(1)–C(22)–Co(2) = 81.5(3).

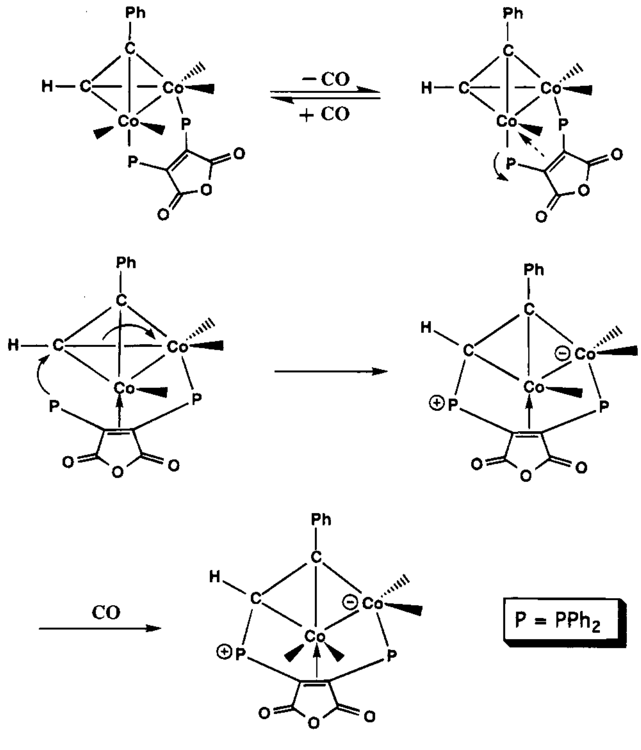


1 (chelating)

1 (bridging)

(2)

Scheme 1



(3)

complexes **2**[4] and PhCCo$_3$(CO)$_7$(bma),[7] we believe that the bridging isomer of **1** serves as an intermediate en route to **3**.[10] When the thermolysis reaction was conducted under CO (100 psi), no reaction was observed and only unreacted **1** (chelating isomer) was isolated. This suggests that dissociative CO loss is a necessary condition for the formation of **1** (bridging isomer) and **3**. An analogous process has been reported for the alkyne–phosphine coupling reaction in binuclear **2**.[4]

The structure of **3** was unequivocally established by X-ray diffraction analysis.[11] Figure 1 shows the ORTEP diagram of **3** and confirms the migration of one of the phosphine moieties associated with the bma ligand to the terminal alkyne carbon of the coordinated phenyl-

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[8] Synthesis and spectroscopic data for **1**: To a Schlenk tube containing 0.1 g (0.26 mmol) of $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$ and 0.13 g (0.27 mmol) of bma was added 20 mL of THF, after which 0.04 g (0.53 mmol) of Me_3NO was added. The reaction mixture was then stirred for 1 h and examined by TLC analysis, which revealed the complete consumption of $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$ and the formation of **1** (chelating isomer). After solvent removal, **1** was then chromatographed over silica gel at −78 °C using CH_2Cl_2/petroleum ether (3:1) as the eluant. The product was recrystallized from CH_2Cl_2/heptane to give 0.13 g (63%) of green-black **1**. IR (CH_2Cl_2): ν(CO) 2048 (vs), 1989 (vs), 1841 (w, asym bma C=O), 1775 (m, sym bma C=O) cm^{-1}. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, room temp): δ 64.6, 54.4 (1P each for pseudo-axial and pseudo-equatorial bma PPh$_2$ groups). Anal. Calcd (found) for $C_{40}H_{26}Co_2O_7P_2 \cdot {}^1/_3CH_2Cl_2$: C, 58.52 (58.59); H, 3.42 (3.25).

[9] Synthesis and spectroscopic data for **3**: To a Schlenk tube containing 0.20 g (0.25 mmol) of $Co_2(CO)_4(bma)(\mu\text{-}PhC{\equiv}CH)$ (chelating isomer) was added 20 mL of 1,2-dichloroethane, after which the solution was heated to reflux for 1 h. TLC and IR analyses indicated the presence of **3** in greater than 90% yield. After solvent removal, **3** was then chromatographed over silica gel using CH_2Cl_2 as the eluant. The product was recrystallized from CH_2Cl_2/heptane to give 0.14 g (70%) of black **3**. IR (CH_2Cl_2): ν(CO) 2035 (s), 2005 (vs), 1983 (m), 1966 (m), 1796 (m, asym bma C=O), 1741 (m, sym bma C=O) cm^{-1}. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −90 °C): δ 31.3 (d, J_{P-P} = 77 Hz, C–P moiety), 4.7 (d, J_{P-P} = 77 Hz, Co–P). ^1H NMR ($CDCl_3$, room temp): δ 4.22 (dd, J_{P-H} = 37.2 Hz and J_{P-H} = 37.2 Hz, zwitterionic C–H, 1H), 7.40 (multiplet, phenyl groups, 25 H). Anal. Calcd (found) for $C_{40}H_{26}Co_2O_7P_2 \cdot {}^1/_2CH_2Cl_2$: C, 57.84 (57.87); H, 3.24 (3.26).

[10] Heating a sealed NMR tube containing **1** (chelating isomer) in 1,2-dichloroethane at 80 °C, followed by quenching and ^{31}P NMR analysis at room temperature, revealed a new ^{31}P chemical shift at δ 25.9. The observed high-field shift of this new resonance is consistent with a bridging bma ligand in **1**.

[11] Crystal data for **3**: $C_{40}H_{26}Co_2O_7P_2$, M_r = 798.46, triclinic space group $P\bar{1}$, a = 9.8093(7) Å, b = 12.215(1) Å, c = 15.744(2) Å, α = 98.251(8)°, β = 95.060(8)°, γ = 90.640(7)°, V = 1859.1(3) Å^3, Z = 2, D_c = 1.426 g/cm^3, $F(000)$ = 812, T = 298 K, μ(Mo Kα) = 10.21 cm^{-1}. Diffraction data were collected in the θ-2θ scan mode (2° < 2θ < 44°). Final R = 0.0365 (R_w = 0.0469) for 2749 unique reflections (with $I > 3\sigma(I)$). The molecular structure was solved by SIR, which revealed the positions of the Co and P atoms. All remaining non-hydrogens were located with difference Fourier maps and full-matrix least-squares refinement. With the exception of the phenyl-ring carbons and hydrogens, all atoms were refined anisotropically. An area of electron density was noted that corresponds to a disordered CH_2Cl_2 solvent molecule of partial occupancy (ϱ_{max} = 1.44 e/Å^3). Since a reasonable model for this solvent molecule could not be developed, it was not included in the final refinement.

acetylene ligand. This regioselective transformation gives rise to the first μ-η^2:η^1-hydrocarbyl ligand complex formed from an intramolecular P-ligand attack on a coordinated alkyne moiety. The zwitterionic nature of **3** requires a negative charge on Co(2) and a positive charge on P(2); the latter center is best described as a phosphonium center, given the tetrasubstituted nature of the P(2) atom. Of interest here is the utilization of the maleic anhydride bond as an η^2-donor ligand in the product, which allows each cobalt center to achieve a coordinatively saturated state.

In comparison to the recently reported work of Takats et al.,[1] which has presented evidence for the formal migration of PMe_3 to a coordinated ethyne ligand, our observation of the formation of **3** from **1** provides the first intramolecular example for such a P-ligand attack sequence. Given the multidentate nature of the bma ligand (i.e., two phosphine and one alkene groups), it is unreasonable to consider a scheme for the formation of **3** that involves the total dissociation of the bma ligand from **1**. Scheme 1 outlines the likely sequence of events leading to **3**, starting from the transient bridging isomer of **1** and invoking a partially dissociated bma ligand as an intermediate. Support for such a scheme derives from related work from our laboratories that has demonstrated the ease by which the bma ligand can dissociate to an η^1-bma ligand during ligand isomerization and activation reactions.[4,7]

The reactivity of other coordinated alkynes in $Co_2(CO)_4$(bma)(μ-alkyne) complexes is being examined, with the aim of elucidating the electronic and steric factors that are operative in the formation of zwitterionic hydrocarbyl-substituted complexes related to **3**.

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Supplementary Material Available: Tables of crystal data, atomic positional parameters and isotropic thermal parameters, bond lengths and bond angles for **3** (16 pages).

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