

Regioselective phosphine attack on the coordinated alkyne
in $\text{Co}_2(\mu\text{-alkyne})$ complexes
Reactivity studies and X-ray diffraction structures
of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C}^t\text{Bu})$ and the zwitterionic hydrocarbyl
complexes
 $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-RC}=\text{C}(\text{R}')\text{PPh}_2\overline{\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})}]$

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Abstract

The alkyne-bridged compounds $\text{Co}_2(\text{CO})_6(\mu\text{-R}'\text{C}\equiv\text{CR})$ (where $\text{R}' = \text{H}$, $\text{R} = \text{Ph}$, ^tBu ; $\text{R}' = \text{Me}$, $\text{R} = \text{Ph}$) have been examined for their reactivity with the redox-active diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma). Thermal and Me_3NO -induced activation of each $\text{Co}_2(\text{CO})_6(\mu\text{-R}'\text{C}\equiv\text{CR})$ compound initially furnishes the binuclear compounds $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-R}'\text{C}\equiv\text{CR})$ (**1c**, $\text{R}' = \text{H}$, $\text{R} = \text{Ph}$; **2c**, $\text{R}' = \text{H}$, $\text{R} = ^t\text{Bu}$; **3c**, $\text{R}' = \text{Me}$, $\text{R} = \text{Ph}$), all of which are shown to possess a chelating bma ligand. These compounds exhibit a reversible chelate-to-bridge bma ligand isomerization that proceeds by a pathway involving dissociative CO loss. The stability of the chelating isomers is dependent on the steric bulk of the alkyne substituents, with the bridging isomer (**1b**, **2b**, **3b**) being favored at ambient temperature only in the case of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C}^t\text{Bu})$ (**2b**). Regioselective phosphine attack at the least-substituted alkyne carbon is observed at temperatures above 60 °C to afford the corresponding zwitterionic hydrocarbyl compounds $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-RC}=\text{C}(\text{R}')\text{PPh}_2\overline{\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})}]$ (**1z**, **2z**, **3z**). Depending on the ease of separation, the new compounds have been characterized by IR and NMR spectroscopy, and the molecular structure of the bridged compound **2b** and all three zwitterionic hydrocarbyl compounds have been determined by X-ray crystallography. **1z** crystallizes in the triclinic space group $P\bar{1}$: $a = 9.8093(7)$ Å, $b = 12.215(1)$ Å, $c = 15.744(2)$ Å, $\alpha = 98.251(8)^\circ$, $\beta = 95.060(8)^\circ$, $\gamma = 90.640(7)^\circ$, $V = 1859.1(3)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.426$ g cm⁻³; $R = 0.0365$, $R_w = 0.0469$ for 2749 observed reflections. **2b** crystallizes in the triclinic space group $P\bar{1}$: $a = 11.1272(7)$ Å, $b = 12.142(1)$ Å, $c = 13.565(1)$ Å, $\alpha = 97.123(7)^\circ$, $\beta = 94.951(6)^\circ$, $\gamma = 100.197(6)^\circ$, $V = 1778.8(2)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.453$ g cm⁻³; $R = 0.0469$, $R_w = 0.0484$ for 3357 observed reflections. **2z** crystallizes in the monoclinic space group $P2_1/n$: $a = 9.465(7)$ Å, $b = 20.071(8)$ Å, $c = 18.389(6)$ Å, $\beta = 98.88(5)^\circ$, $V = 3452(3)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.498$ g cm⁻³; $R = 0.0544$, $R_w = 0.0589$ for 3114 observed reflections. **3z**, as the CH_2Cl_2 solvate, crystallizes in the triclinic space group $P\bar{1}$: $a = 9.732(3)$ Å, $b = 12.286(2)$ Å, $c = 16.715(3)$ Å, $\alpha = 98.39(1)^\circ$, $\beta = 102.91(2)^\circ$, $\gamma = 91.93(2)^\circ$, $V = 1922.6(8)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.550$ g cm⁻³; $R = 0.0730$, $R_w = 0.0825$ for 2896 observed reflections. The X-ray data on **1z**, **2z**, and **3z** confirm the site of phosphine attack on the coordinated alkyne ligand and the presence of the eight-electron hydrocarbyl ligand that accompanies this reaction. The redox properties of the zwitterionic compounds $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-RC}=\text{C}(\text{R}')\text{PPh}_2\overline{\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})}]$ have been examined by cyclic voltammetry, and the data discussed relative to the coordination mode adopted by the bma ligand and the redox properties exhibited by the related alkyne-bridged compound $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ (chelating and bridging isomers). Extended Hückel calculations on the model compound $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-HC}=\text{C}(\text{H})\text{PPh}_2\overline{\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})}]$ have been carried out and are used in a discussion concerning the site of electron reduction and oxidation in **1z**, **2z**, and **3z**.

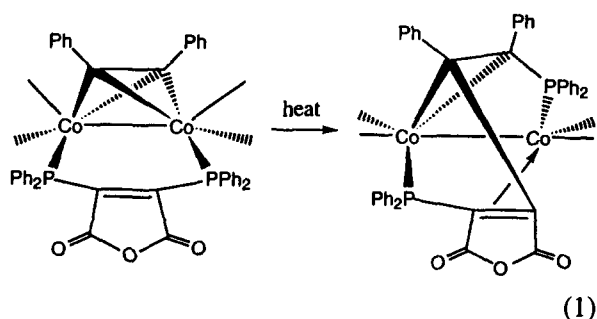
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1. Introduction

Alkyne-substituted transition metal compounds have been shown to function as versatile intermediates in the synthesis of a variety of pharmaceutically important natural products and afford commodity chemicals that serve as basic building blocks of more complex molecules [1,2]. Undoubtedly, the best known organic synthetic reactions involving metal–alkyne compounds are based on the dicobalt system $\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})$ and include the Pauson–Khand and the Nicholas reactions, which derive their immense utility from the construction of complex carbocyclic rings and the stereocontrolled formation of carbon–carbon bonds using propargyl cation synthons respectively [3–5].

Recently, we have reported our findings on the reactivity and redox chemistry of the alkyne-bridged compounds $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ (bridging and chelating isomers) that contain the ancillary redox-active ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma) [6,7]. The unique properties of the bma ligand in these compounds have been demonstrated by (1) cyclic voltammetry experiments [8], (2) the reversible chelate-to-bridge bma ligand exchange observed at ambient temperature, and (3) the P–C(maleic anhydride) bond activation and alkyne coupling that originates from the bridged bma isomer, as shown in Eq. (1).



As a continuation of the $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ work, we next examined the reactivity of the alkyne complex $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{CPh})$, fully expecting a similar course of reactivity as found for the diphenylacetylene derivative. However, it was shown that one of the phosphine groups attacks the terminal alkyne carbon at elevated temperature to give the zwitterionic hydrocarbyl complex $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-PhC}\equiv\text{C(H)PPh}_2\text{C}\equiv\text{C(PPh}_2\text{)C(O)OC(O)}]$. A portion of this work has already been communicated [9]. This reaction represents the first known example of an intramolecular phosphine ligand attack on a coordinated alkyne ligand [10].

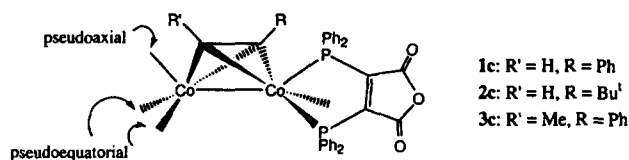
Herein we present our results on the synthesis of the chelated bma compounds $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-R}'\text{C}\equiv\text{CR})$ (**1c**, **2c**, **3c**) and the isomerization of these compounds

to the corresponding bridging compounds (**1b**, **2b**, **3b**). Thermolysis of isomeric mixtures of **1c,b** and **3c,b** and isomerically pure **2b** yields the zwitterionic hydrocarbyl compounds $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-RC}\equiv\text{C(R')PPh}_2\text{-C}\equiv\text{C(PPh}_2\text{)C(O)OC(O)}]$ (**1z**, **2z**, **3z**), as a result of phosphine attack at the least sterically hindered alkyne carbon. X-ray crystallography has unequivocally established the site of phosphine attack in each of the zwitterionic hydrocarbyl compounds. The electron reservoir properties of **1z**, **2z**, and **3z** are shown by cyclic voltammetry studies and extended Hückel MO calculations to be modulated by the coordinated bma ligand. An electrochemical comparison of **1z**, **2z**, and **3z** with the bma-substituted compounds $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-R}'\text{C}\equiv\text{CR})$ (chelating and bridging isomers) and the parent binuclear compound $\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})$ underscores the participation of the redox-active bma ligand in helping to tune the redox potential of the $0/1^-$ redox couple and stabilizing the product of one-electron reduction.

2. Results and discussion

2.1. Synthesis and solution characterization

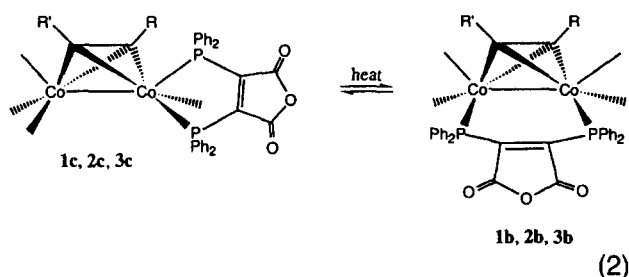
The chelated bma compounds **1c**, **2c**, and **3c** may be obtained in moderate to good yield by treating the parent hexacarbonyl compounds $\text{Co}_2(\text{CO})_6(\mu\text{-R}'\text{C}\equiv\text{CR})$ [11] with bma and 2 equivalents of the oxidative-decarbonylation reagent Me_3NO [12]. Thermolysis (below 50°C) of $\text{Co}_2(\text{CO})_6(\mu\text{-R}'\text{C}\equiv\text{CR})$ in the presence of bma also affords the same chelated bma compounds, $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-R}'\text{C}\equiv\text{CR})$, in yields that are highly dependent on the steric nature of the alkyne substituents, with the equilibration of the initially formed chelating isomer to the bridging isomer representing the predominant side reaction in the case of the isomeric pair **2c/2b**. Phosphine substitution at a pseudoaxial and pseudoequatorial site in **1c**, **2c**, and **3c** (shown below) is assured, on the basis of the spectral data given in Table 1.



Consistent with the chelated bma ligand in **1c**, **2c**, and **3c** is the observation of two terminal $\nu(\text{CO})$ bands, in addition to the expected two $\nu(\text{CO})$ bands belonging to the bma ligand [6,9]. In the case of the unsymmetrical alkynes employed in this work, it is anticipated that phosphine substitution at the inequivalent pseudoequatorial sites takes place at a distal pseudoequatorial site relative to the larger R substituent [13,14]. Further

spectroscopic proof for the existence of a chelated bma ligand in each of these compounds derives from the two inequivalent ^{31}P NMR resonances observed at ca. δ 65 and 55 for the pseudoaxial and pseudoequatorial PPh_2 groups. ^{13}C -enriched samples of **1c**, **2c**, and **3c** were also examined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy in order to establish the ligation mode of the bma ligand. At -90°C all three of these compounds exhibit two carbonyl resonances at ca. δ 202 and 207, assignable to the $\text{Co}(\text{CO})_3$ moiety and the lone CO group at the bma-chelated cobalt center respectively [6]. Warming these two samples to room temperature led only to the broadening of these resonances as a result of increased ^{13}C - ^{59}Co scalar coupling [15]. The observation of only one carbonyl resonance for the $\text{Co}(\text{CO})_3$ center suggests that either the three CO groups are magnetically degenerate, which seems unlikely, or that rapid three-fold carbonyl scrambling remains facile at the lowest temperature investigated. The latter explanation gains strength from the fact that facile three-fold scrambling is observed at $\text{Co}(\text{CO})_3$ vertices in tetrahedral clusters [15,16].

Heating a solution containing **1c**, **2c**, or **3c** leads to the formation of the bridged bma isomers **1b**, **2b**, and **3b**, as depicted by Eq. (2).



The amount of bridging isomer formed is highly dependent on the steric crowding present between the alkyne and bma ligands. For example, heating a 1,2-dichloroethane solution containing either **2c** or **3c** at 45°C gave the corresponding bma-bridged isomer in 90% and 20% yield respectively. Similar data were obtained for these two samples when heated in CH_2Cl_2 and analyzed by ^{31}P NMR analysis. That this reaction truly

Table 1
Spectroscopic data of the new alkyne and zwitterionic compounds

| | IR (cm^{-1}) ^a terminal and bma CO groups | $^{31}\text{P}\{^1\text{H}\}$ NMR (δ) ^b | $^{13}\text{C}\{^1\text{H}\}$ NMR (δ) ^b terminal CO groups | ^1H NMR (δ) ^c |
|-----------|---|---|--|---|
| 1c | 2048 (vs), 1989 (vs), 1841 (w, asym bma C=O), 1775 (m, sym bma C=O) | 64.61, 54.38 | 201.84 (3C), 206.86 (1C) | 5.77 (d, HC \equiv , $J_{\text{P-H}} = 10.54$ Hz), 7.50 (m, Ph groups) |
| 1b | — | 25.90 ^d | — | — |
| 1z | 2035 (s), 2005(vs), 1983 (m), 1966 (m), 1796 (m, asym bma C=O), 1741 (m, sym, bma) | 31.30 (d, $J_{\text{P-P}} = 77$ Hz, C-P), 4.70 (d, $J_{\text{P-P}} =$ 77 Hz, Co-P) | 201.15 (d, 1C, $J_{\text{P-C}} = 20$ Hz), 203.17 (1C), 203.96 (1C), 208.15 (1C) | 4.22 (dd, $\text{Ph}_2\text{PCH}=\text{C}$, $J_{\text{P-H}} = 7$ Hz, $J_{\text{P-H}} = 37$ Hz), 7.40 (m, Ph groups) |
| 2c | 2044 (vs), 1982 (vs), 1840 (w, asym bma C=O), 1774 (m, sym bma C=O) | 66.73, 55.73 | 202.40 (3C), 207.65 (1C) | 1.08 (^t Bu), 5.34 (dd, HC \equiv , $J_{\text{P-H}} =$ 3 Hz, $J_{\text{P-H}} = 9$ Hz), 7.50 (m, Ph groups) |
| 2b | 2026 (s), 1997 (vs), 1972 (s) 1818 (w, asym bma C=O), 1767 (m, sym bma C=O) | 28.14 | 201.89 (2C), 207.60 (2C) | 1.35 (^t Bu), 5.41 (t, HC \equiv , $J_{\text{P-H}} =$ 9 Hz), 7.25 (b, Ph groups) |
| 2z | 2034 (s), 1999 (vs), 1981 (s, sh), 1961 (s), 1796 (m, asym bma, C=O), 1738 (m, sym, bma) | 28.78 (d, $J_{\text{P-P}} = 82$ Hz, C-P), 5.64 (d, $J_{\text{P-P}} =$ 82 Hz, Co-P) | 202.93 (d, 1C, $J_{\text{P-C}} = 20$ Hz), 204.17 (1C), 204.89 (1C), 209.99 (1C) | 1.41 (^t Bu), 3.92 (dd, $\text{Ph}_2\text{PCH}=\text{C}$, $J_{\text{P-H}} = 8$ Hz, $J_{\text{P-H}} = 44$ Hz), 7.40 (m, Ph groups) |
| 3c | 2043 (s), 1984 (vs), 1841 (w, asym bma C=O), 1775 (m, sym bma C=O) | 63.49, 56.87 | 202.42 (3C), 206.98 (1C) | 1.95 (Me), 7.43 (m, Ph groups) |
| 3b | 2029 (s), 2004 (s), 1975 (s) ^e | 29.76 ^f | 200.84 (3C), 204.92 (1C) ^f | 2.74 (Me), 7.35 (m, Ph groups) ^f |
| 3z | 2033 (s), 2001 (vs) 1983 (m), 1962 (m) 1794 (m, asym bma C=O), 1738 (m, sym bma C=O) | 39.65 (d, $J_{\text{P-P}} = 73$ Hz, C-P), 10.87 (d, $J_{\text{P-P}} =$ 73 Hz, Co-P) | 202.21 (d, 1C, $J_{\text{P-C}} = 19$ Hz), 202.99 (1C), 203.31 (1C), 208.34 (1C) | 1.86 (d, Me, $J_{\text{P-H}} =$ 14 Hz), 7.30 (m, Ph groups) |

^a All IR spectra were recorded in CH_2Cl_2 . ^b All ^{31}P and ^{13}C NMR spectra were recorded in CH_2Cl_2 at -90°C . ^c All ^1H NMR spectra were recorded in CDCl_3 at room temperature. ^d $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded at room temperature. The reported data were obtained from a sample of **1c** that had been heated in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$. ^e IR data obtained from a mixture of chelating and bridging isomers using spectral subtraction techniques. IR data for the bma $\nu(\text{CO})$ bands could not be obtained owing to their weak intensity and extensive overlap with the chelating isomer. ^f NMR data obtained from a thermally equilibrated samples of **3c** and **3b**.

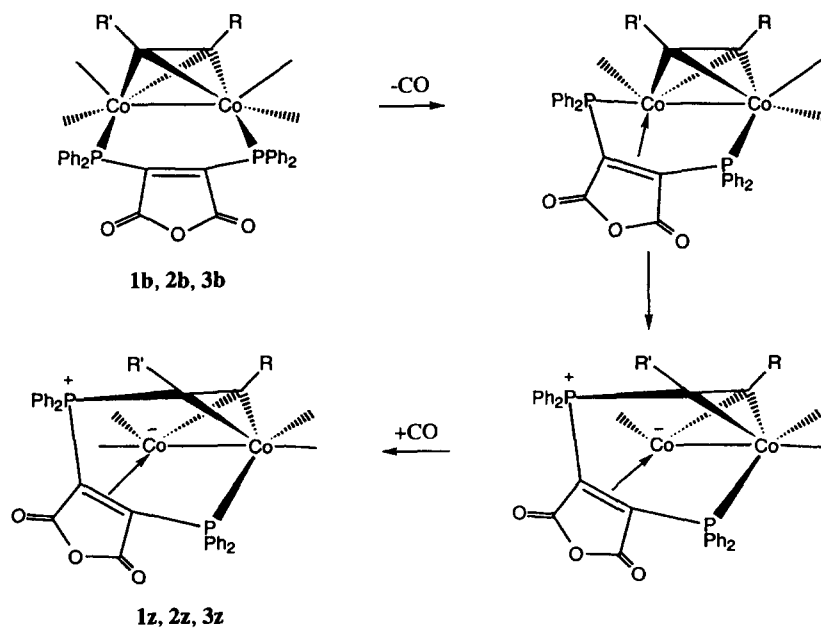
reflects an equilibrium was shown by the thermolysis of **2b** in 1,2-dichloroethane at 45 °C. Here, after 24 h, the ^{31}P NMR spectrum revealed a 10% conversion to the chelating isomer **2c**, in full agreement with the $K_{\text{eq}} = 9$ found when starting from **2c**. For comparison, the binuclear compound $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ gave a $K_{\text{eq}}(\text{bridge}/\text{chelate}) \sim 1$ at 45 °C [6]. The sterically less demanding phenylacetylene ligand in **1c** shows no evidence for isomerization under these conditions, as only **1c** was recovered even after extensive thermolysis at 45 °C. Refluxing a sample of **1c** in 1,2-dichloroethane, followed by quenching and ^{31}P NMR analysis, did reveal the presence of **2b** (less than 2%) by its characteristic high-field ^{31}P chemical shift at δ 25.90 [9]. The chelate-to-bridge isomerization reaction depicted by Eq. (2) proceeds by a pathway involving dissociative CO loss, given that thermolysis reactions under 100 lbf in $^{-2}$ of CO gave only unreacted chelating isomer. The bma isomerization chemistry exemplified by the binuclear compounds presented here and $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ [6] stands in contrast to that reported for the tricobalt cluster $\text{PhCCO}_3(\text{CO})_7(\text{bma})$, in which the bma ligand scrambles about the cluster polyhedron without CO loss [7].

Only in the case of **2** were we able to efficiently separate the two bma isomers. The pertinent spectroscopic data for **2b** are given in Table 1. The solution IR and NMR data for **1b** and **3b** are also reported in Table 1 and derive from the in situ characterization of isomeric mixtures. Diagnostic of the bma-bridged isomers is the single, high-field ^{31}P chemical shift observed for each compound at ca. δ 26–30. From Eq. (2) it is seen that the bma ligand adopts a pseudoequatorial site at each cobalt center that features a minimum amount of

steric hindrance with the two alkyne substituents (vide infra).

Attack of one of the PPh_2 moieties on the coordinated alkyne ligand to furnish the zwitterionic hydrocarbyl compounds **1z**, **2z**, and **3z** was achieved by refluxing the chelating and bridging isomers of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-R}'\text{C}\equiv\text{CR})$ in 1,2-dichloroethane or toluene solvent. This reaction proceeds cleanly with only minimal material loss, and isolated yields were on the order of 70%. All of these hydrocarbyl compounds exhibit $\nu(\text{CO})$ bands for the terminal cobalt-carbonyl and bma groups that are frequency insensitive. The ^{31}P NMR spectral data all reveal the presence of two ^{31}P doublets ($J_{\text{P-P}} \approx 77$ Hz), with the lower field resonance being assigned to the alkyne-substituted phosphine moiety because only the phosphine moiety attached to the cobalt center exhibits pronounced temperature-dependent behavior, the origin of which derives from ^{13}C – ^{59}Co scalar coupling [15].

Scheme 1 shows the probable steps involved for the formation of the hydrocarbyl compounds **1z**, **2z**, and **3z**, starting from the bridged-bma isomers. The initial step in this transformation involving the dissociative loss of CO from the bridged-bma isomer is supported by experiments conducted under CO (100 lbf in $^{-2}$), which effectively suppressed the formation of **1z**, **2z**, and **3z**. Coordination of the maleic anhydride π bond after CO loss gives the first intermediate in Scheme 1. Intramolecular attack of the PPh_2 group associated with the maleic anhydride substituted cobalt center at the least-substituted alkyne carbon, coupled with concomitant Co–C(alkyne) bond cleavage, and CO coordination complete the reaction. With these three examples, we are able to demonstrate that phosphine attack on an



Scheme 1.

alkyne ligand is feasible and occurs under relatively mild reaction conditions. While the full exploitation of this type of alkyne activation remains to be established, we note that the nature of the ancillary diphosphine is crucial in determining the success of this reaction. The diphosphine-substituted compound $\text{Co}_2(\text{CO})_4[(Z)\text{-Ph}_2\text{-PCH=CHPh}_2](\mu\text{-PhC}\equiv\text{CH})$ (chelating isomer) does not show any signs of isomerization or alkyne attack when examined under comparable conditions [17]. As expected, a steric threshold exists for this reaction. Use of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ leads to the oxidative addition of the P–C(maleic anhydride) bond and coupling of the maleic anhydride derived alkenyl group with the alkyne moiety (Eq. (1)) [6]. We are currently examining the possible utilization of the hydrocarbyl compounds **1z** and **2z** as precursors to alkenyl-based ylido compounds.

2.2. X-ray diffraction structures for **1z**, **2b**, **2z**, and **3z**

The molecular structures of the three zwitterionic hydrocarbyl compounds **1z**, **2z**, and **3z** and the bma-bridged compound **2b** were determined by X-ray diffraction analysis. All of these compounds exist as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters are given in Table 2, with Tables 3 and 4 respectively containing the final

positional parameters and selected bond distances and angles. The disposition of the bma ligand in each compound is seen in the ORTEP diagrams shown in Fig. 1.

The bridging isomer of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C-}^t\text{Bu})$, **2b**, possesses a $\text{Co}_2(\mu\text{-alkyne})$ tetrahedral core, as is commonly found in this genre of compound, and displays a Co–Co bond length of 2.466(1) Å, which is unremarkable in comparison with other structurally characterized $\text{Co}_2(\mu\text{-alkyne})$ compounds [18]. The remaining distances and angles are unexceptional and require no comment.

The ORTEP diagram of **2b** confirms the positioning of the bma ligand at the pairwise equivalent pseudoequatorial sites that are distal with respect to the large ^tBu group. Substitution of the bma ligand at the two pseudoequatorial sites located syn to the ^tBu group would certainly lead to destabilizing diphosphine–alkyne contacts. Unfortunately, we were unable to grow single crystals of **2c**, which would have allowed us to explore the diphosphine–alkyne interactions present in the chelating isomer. However, the equilibration of **2c** to **2b** suggests that the chelating isomer experiences some degree of steric destabilization and transforms into the more favorable bma-bridged conformation. This is reasonable when one considers that the PPh_2 moiety occupying the pseudoaxial site in **2c** would be closer to the ^tBu group than in the bridged isomer, and we believe

Table 2
X-ray crystallographic data and processing parameters for compounds **1z**, **2b**, **2z**, and **3z**

| | 1z | 2b | 2z | 3z |
|---|---|---|---|--|
| Space group | $P\bar{1}$, triclinic | $P\bar{1}$, triclinic | $P2_1/n$, monoclinic | $P\bar{1}$, triclinic |
| <i>a</i> (Å) | 9.8093(7) | 11.1272(7) | 9.465(7) | 9.732(3) |
| <i>b</i> (Å) | 12.215(1) | 12.142(1) | 20.071(8) | 12.286(2) |
| <i>c</i> (Å) | 15.744(2) | 13.565(1) | 18.389(6) | 16.715(3) |
| α (deg) | 98.251(8) | 97.123(7) | | 98.39(1) |
| β (deg) | 95.060(8) | 94.951(6) | 98.88(5) | 102.91(2) |
| γ (deg) | 90.640(7) | 100.197(6) | | 91.93(2) |
| <i>V</i> (Å ³) | 1859.1(3) | 1778.8(2) | 3452(3) | 1922.6(8) |
| Mol formula | $\text{C}_{40}\text{H}_{26}\text{Co}_2\text{O}_7\text{P}_2$ | $\text{C}_{38}\text{H}_{30}\text{Co}_2\text{O}_7\text{P}_2$ | $\text{C}_{38}\text{H}_{30}\text{Co}_2\text{O}_7\text{P}_2$ | $\text{C}_{42}\text{H}_{30}\text{Cl}_2\text{Co}_2\text{O}_7\text{P}_2$ |
| Fw | 798.46 | 778.47 | 778.47 | 897.42 |
| Formula units per cell (<i>Z</i>) | 2 | 2 | 4 | 2 |
| ρ (g cm ⁻³) | 1.426 | 1.453 | 1.498 | 1.550 |
| Abs coeff (μ) (cm ⁻¹) | 10.21 | 10.65 | 10.98 | 11.33 |
| λ (Mo K α) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Collection range (deg) | $2.0 \leq 2\theta \leq 44.0$ | $2.0 \leq 2\theta \leq 44.0$ | $2.0 \leq 2\theta \leq 44.0$ | $2.0 \leq 2\theta \leq 44.0$ |
| Total no. of data collected | 4605 | 4347 | 4688 | 4701 |
| No. of indep data | 2749 | 3357 | 3114 | 2896 |
| $I > 3\sigma(I)$ | | | | |
| <i>R</i> | 0.0365 | 0.0469 | 0.0544 | 0.0730 |
| <i>R_w</i> | 0.0469 | 0.0484 | 0.0589 | 0.0825 |
| GOF | 1.76 | 1.18 | 1.58 | 1.28 |
| Weights | $[0.04F^2 + (\sigma F)^2]^{-1}$ | $[0.04F^2 + (\sigma F)^2]^{-1}$ | $[0.04F^2 + (\sigma F)^2]^{-1}$ | $[0.04F^2 + (\sigma F)^2]^{-1}$ |

that it is this interaction between the pseudoaxial PPh₂ moiety and the alkyne substituents that controls, in large part, the degree of bma isomerization. In comparison with **2c**, **1c** resists isomerization to **1b** owing to the presence of the less sterically demanding phenyl group; compound **3c**, which differs from **1c** by its methyl

substituent, exhibits an analogous preference for a chelated bma ligand.

All of the hydrocarbyl compounds are derived by attack of one of the PPh₂ groups at the least-substituted alkyne carbon, as shown in the ORTEP diagrams of **1z**, **2z**, and **3z**. The Co–Co bond lengths found for com-

Table 3

Positional parameters for the non-hydrogen atoms in compounds **1z**, **2b**, **2z**, and **3z** with estimated standard deviations in parentheses ^a

| Atom | x | y | z | B, (Å ²) |
|--|-----------|------------|------------|----------------------|
| Co ₂ (CO) ₄ [μ-η ² :η ² :η ¹ :η ¹ -PhC=C(H)PPh ₂ C≡C(PPh ₂)C(O)OC(O)] (1z) | | | | |
| Co(1) | 0.5130(1) | 0.18010(9) | 0.14694(6) | 2.71(2) |
| Co(2) | 0.2836(1) | 0.23646(9) | 0.20220(7) | 2.80(2) |
| P(1) | 0.5420(2) | 0.2016(2) | 0.2888(1) | 2.76(4) |
| P(2) | 0.4635(2) | 0.4335(2) | 0.1868(1) | 2.72(4) |
| O(1) | 0.4391(7) | -0.0522(5) | 0.0889(5) | 6.3(2) |
| O(2) | 0.7817(6) | 0.1701(6) | 0.0826(4) | 5.8(2) |
| O(3) | 0.1709(7) | 0.0141(5) | 0.2058(5) | 6.7(2) |
| O(4) | 0.0214(6) | 0.3217(6) | 0.1469(5) | 6.9(2) |
| O(12) | 0.3402(6) | 0.2748(5) | 0.4578(3) | 5.4(2) |
| O(13) | 0.2575(5) | 0.4086(5) | 0.3897(3) | 3.7(1) |
| O(14) | 0.2139(5) | 0.5308(5) | 0.2982(4) | 4.5(1) |
| C(1) | 0.4675(8) | 0.0385(7) | 0.1123(5) | 4.1(2) |
| C(2) | 0.6785(8) | 0.1722(7) | 0.1108(5) | 3.7(2) |
| C(3) | 0.2184(8) | 0.0987(8) | 0.2056(5) | 4.0(2) |
| C(4) | 0.1227(9) | 0.2888(7) | 0.1718(5) | 4.0(2) |
| C(11) | 0.4022(7) | 0.2924(6) | 0.3147(5) | 2.8(2) |
| C(12) | 0.3367(8) | 0.3166(7) | 0.3945(5) | 3.4(2) |
| C(14) | 0.2752(7) | 0.4504(7) | 0.3130(5) | 3.3(2) |
| C(15) | 0.3696(7) | 0.3794(6) | 0.2652(5) | 2.6(2) |
| C(21) | 0.4727(7) | 0.3239(6) | 0.1021(5) | 2.9(2) |
| C(22) | 0.3623(7) | 0.2446(6) | 0.0899(4) | 2.6(2) |
| C(23) | 0.2886(7) | 0.2077(6) | 0.0025(5) | 3.1(2) * |
| C(24) | 0.3160(9) | 0.2551(8) | -0.0691(6) | 5.1(2) * |
| C(25) | 0.246(1) | 0.2178(9) | -0.1492(7) | 6.4(3) * |
| C(26) | 0.150(1) | 0.1363(9) | -0.1584(6) | 5.7(2) * |
| C(27) | 0.121(1) | 0.0884(9) | -0.0903(7) | 5.7(2) * |
| C(28) | 0.1925(9) | 0.1210(8) | -0.0088(6) | 4.9(2) * |
| C(111) | 0.6946(7) | 0.2607(6) | 0.3540(5) | 3.0(2) * |
| C(112) | 0.8098(9) | 0.2736(8) | 0.3179(6) | 4.7(2) * |
| C(113) | 0.932(1) | 0.320(1) | 0.3688(8) | 73(3) * |
| C(114) | 0.930(1) | 6.347(1) | 0.4555(7) | 7.1(3) * |
| C(115) | 0.811(1) | 0.3317(9) | 0.4923(7) | 6.4(3) * |
| C(116) | 0.6931(9) | 0.2875(8) | 0.4412(6) | 4.6(2) * |
| C(117) | 0.5190(7) | 0.0722(6) | 0.3338(5) | 3.1(2) * |
| C(118) | 0.4045(9) | 0.0416(8) | 0.3691(6) | 4.9(2) * |
| C(119) | 0.399(1) | -0.0647(9) | 0.3966(7) | 6.2(2) * |
| C(120) | 0.509(1) | -0.1302(8) | 0.3904(6) | 5.4(2) * |
| C(121) | 0.619(1) | -0.1017(9) | 0.3568(7) | 5.9(2) * |
| C(122) | 0.626(1) | 0.0011(8) | 0.3289(6) | 5.2(2) * |
| C(211) | 0.6286(7) | 0.4895(6) | 0.2321(5) | 3.0(2) * |
| C(212) | 0.6443(9) | 0.5397(7) | 0.3194(5) | 4.2(2) * |
| C(213) | 0.7687(9) | 0.5895(8) | 0.3526(6) | 4.8(2) * |
| C(214) | 0.8741(9) | 0.5876(8) | 0.3050(6) | 5.1(2) * |
| C(215) | 0.8604(9) | 0.5369(8) | 0.2201(6) | 4.8(2) * |
| C(216) | 0.7386(8) | 0.4879(7) | 0.1839(5) | 4.1(2) * |
| C(217) | 0.3678(8) | 0.5459(6) | 0.1501(5) | 3.1(2) * |
| C(218) | 0.2664(9) | 0.5209(7) | 0.0849(6) | 4.3(2) * |
| C(219) | 0.184(1) | 0.6100(9) | 0.0603(7) | 6.0(2) * |
| C(220) | 0.209(1) | 0.7154(9) | 0.0997(7) | 6.4(3) * |
| C(221) | 0.314(1) | 0.7367(9) | 0.1640(7) | 5.9(2) * |
| C(222) | 0.3933(9) | 0.6530(8) | 0.1892(6) | 5.0(2) * |

pounds **1z** (2.549(1) Å), **2z** (2.564(1) Å), and **3z** (2.548(2) Å) are only slightly longer than that reported for $\text{Co}_2(\mu\text{-alkyne})$ compounds [18]. The maleic anhydride π bond is coordinated at the cobalt center that bears the formal anionic charge required by the zwitterionic nature of each compound, while the P(2) atom of each compound bears a positive charge consistent with its description as a phosphonium group given its tetrahedral character. The anionic charge at each Co(2) center is stabilized by the electron-withdrawing maleic

anhydride ring, whose electron-withdrawing properties have been demonstrated by its promotion of heterolytic Co–Co bond cleavage in tricobalt clusters examined by our groups [19]. All other bond distances and angles are normal.

2.3. Cyclic voltammetry (CV) data

The electrochemical properties of all the hydrocarbyl compounds and pure **1c**, **2b**, and **3c** were explored by

Table 3 (continued)

| Atom | x | y | z | B, (Å ²) |
|--|------------|------------|------------|----------------------|
| $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C}^i\text{Bu})$ (bridging isomer) (2b) | | | | |
| Co(1) | 0.26615(7) | 0.21324(6) | 0.16138(6) | 3.08(2) |
| Co(2) | 0.25616(7) | 0.10335(6) | 0.30259(6) | 2.88(2) |
| P(1) | 0.2431(1) | 0.3853(1) | 0.2234(1) | 2.92(3) |
| P(2) | 0.2079(1) | 0.2220(1) | 0.4238(1) | 2.87(3) |
| O(1) | 0.5329(4) | 0.2461(4) | 0.1585(4) | 6.6(1) |
| O(2) | 0.1791(6) | 0.2445(5) | −0.0394(4) | 7.1(2) |
| O(3) | 0.1585(6) | −0.1024(4) | 0.3802(5) | 8.4(2) |
| O(4) | 0.5175(4) | 0.1099(5) | 0.3509(4) | 7.2(2) |
| O(12) | 0.3627(4) | 0.6369(3) | 0.3644(3) | 4.9(1) |
| O(13) | 0.3794(4) | 0.5545(3) | 0.5018(3) | 3.69(9) |
| O(14) | 0.3388(5) | 0.4325(4) | 0.6098(3) | 5.2(1) |
| C(1) | 0.4293(6) | 0.2366(5) | 0.1609(5) | 4.2(2) |
| C(2) | 0.2138(6) | 0.2319(6) | 0.0391(5) | 4.5(2) |
| C(3) | 0.1964(6) | −0.0199(6) | 0.3511(5) | 4.7(2) |
| C(4) | 0.4157(6) | 0.1098(6) | 0.3335(5) | 4.2(2) |
| C(11) | 0.2952(5) | 0.4324(4) | 0.3565(4) | 2.7(1) |
| C(12) | 0.3492(5) | 0.5525(5) | 0.4001(5) | 3.5(1) |
| C(14) | 0.3346(5) | 0.4479(5) | 0.5261(4) | 3.4(1) |
| C(15) | 0.2824(5) | 0.3716(5) | 0.4317(4) | 2.7(1) |
| C(16) | 0.1313(3) | 0.0981(5) | 0.1895(4) | 3.4(1) |
| C(17) | 0.2233(5) | 0.0487(5) | 0.1582(4) | 3.5(1) |
| C(18) | 0.2443(6) | −0.0528(5) | 0.0903(5) | 4.5(2) |
| C(19) | 0.3752(8) | −0.0622(7) | 0.0981(7) | 8.6(2) |
| C(20) | 0.169(1) | −0.1583(7) | 0.1184(8) | 10.7(3) |
| C(21) | 0.203(1) | −0.0421(8) | −0.0160(7) | 11.6(3) |
| C(111) | 0.3375(5) | 0.4897(5) | 0.1627(4) | 3.1(1) * |
| C(112) | 0.4628(5) | 0.5164(5) | 0.1905(4) | 3.5(1) * |
| C(113) | 0.5374(6) | 0.5905(5) | 0.1418(5) | 4.0(1) * |
| C(114) | 0.4881(6) | 0.6349(6) | 0.0647(5) | 4.8(1) * |
| C(115) | 0.3657(6) | 0.6071(6) | 0.0342(5) | 4.7(1) * |
| C(116) | 0.2879(6) | 0.5350(5) | 0.0830(5) | 3.9(1) * |
| C(117) | 0.0927(5) | 0.4258(5) | 0.2177(4) | 3.5(1) * |
| C(118) | −0.0105(6) | 0.3422(6) | 0.1927(5) | 4.8(1) * |
| C(119) | −0.1277(8) | 0.3691(7) | 0.1928(6) | 6.4(2) * |
| C(120) | −0.1380(8) | 0.4777(7) | 0.2191(6) | 6.7(2) * |
| C(121) | −0.0380(8) | 0.5628(7) | 0.2421(6) | 6.7(2) * |
| C(122) | 0.0801(6) | 0.5368(6) | 0.2433(5) | 4.9(2) * |
| C(211) | 0.0482(5) | 0.2380(5) | 0.4238(4) | 3.0(1) * |
| C(212) | −0.0436(6) | 0.1500(5) | 0.3804(5) | 3.9(1) * |
| C(213) | −0.1669(6) | 0.1583(6) | 0.3816(5) | 4.9(1) * |
| C(214) | −0.1974(7) | 0.2538(6) | 0.4272(5) | 5.2(2) * |
| C(215) | −0.1071(7) | 0.3401(6) | 0.4746(6) | 5.7(2) * |
| C(216) | 0.0164(6) | 0.3329(6) | 0.4729(5) | 4.8(1) * |
| C(217) | 0.2474(5) | 0.1901(5) | 0.5496(4) | 3.3(1) * |
| C(218) | 0.3675(6) | 0.1819(5) | 0.5778(5) | 4.3(1) * |
| C(219) | 0.4013(7) | 0.1574(6) | 0.6733(6) | 5.5(2) * |
| C(220) | 0.3150(7) | 0.1397(6) | 0.7362(6) | 5.6(2) * |
| C(221) | 0.1958(7) | 0.1445(6) | 0.7106(6) | 5.6(2) * |
| C(222) | 0.1597(6) | 0.1703(6) | 0.6158(5) | 4.5(1) * |

CV at a platinum electrode in solutions containing 0.2 M TBAP as the supporting electrolyte. Our CV studies involving the chelating and bridging bma isomers of **1–3** were restricted to those compounds that could be isolated free from isomer contamination. **1c**, **2b**, and **3c** all exhibited two reversible reductions assignable to the $0/1^-$ and $1^-/2^-$ redox couples in CH_2Cl_2 , along with a quasi-reversible $0/1^+$ redox couple; the potential data

for **1c**, **2b**, and **3c** closely matched those reported for bma isomers of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$, whose electrochemistry has been fully discussed [6].

A detailed discussion of the electrochemical properties of **1z**, **2z**, and **3z** will be restricted to the hydrocarbyl compound **3z**, since all three compounds exhibit similar electrochemistry. **3z** exhibits two well-defined reductions in THF at $E_{1/2} = -1.28$ and $E_{1/2} = -1.46$

Table 3 (continued)

| Atom | x | y | z | B, (Å ²) |
|---|-----------|------------|------------|----------------------|
| $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-}^t\text{BuC}=\text{C}(\text{H})\text{PPh}_2\text{C}=\text{C}(\text{O})\text{OC}(\text{O})]$ (2z) | | | | |
| Co(1) | 1.2432(1) | 0.09082(5) | 0.82140(6) | 3.40(2) |
| Co(2) | 0.9743(1) | 0.11445(5) | 0.80912(6) | 3.48(2) |
| P(1) | 1.1392(2) | 0.0155(1) | 0.7453(1) | 3.06(4) |
| P(2) | 1.1022(2) | 0.1844(1) | 0.6885(1) | 3.30(4) |
| O(1) | 1.3064(9) | 0.0363(4) | 0.9693(3) | 8.1(2) |
| O(2) | 1.5413(7) | 0.0845(4) | 0.8026(5) | 8.3(2) |
| O(3) | 0.9071(8) | 0.0361(4) | 0.9313(4) | 9.0(2) |
| O(4) | 0.7413(7) | 0.2015(3) | 0.8328(4) | 7.7(2) |
| O(12) | 0.7860(6) | -0.0279(3) | 0.6888(4) | 6.0(2) |
| O(13) | 0.7389(5) | 0.0786(3) | 0.6559(3) | 4.4(1) |
| O(14) | 0.7601(6) | 0.1843(3) | 0.6244(4) | 6.0(2) |
| C(1) | 1.274(1) | 0.0584(5) | 0.9113(5) | 5.0(2) |
| C(2) | 1.4245(9) | 0.0856(4) | 0.8091(5) | 4.9(2) |
| C(3) | 0.938(1) | 0.0647(5) | 0.8819(5) | 5.4(2) |
| C(4) | 0.8337(9) | 0.1668(4) | 0.8220(5) | 4.9(2) |
| C(11) | 0.9692(7) | 0.0572(4) | 0.7146(4) | 3.0(2) |
| C(12) | 0.8327(8) | 0.0272(4) | 0.6881(4) | 4.1(2) |
| C(14) | 0.8157(8) | 0.1382(4) | 0.6564(4) | 4.1(2) |
| C(15) | 0.9609(7) | 0.1273(4) | 0.6985(4) | 3.1(2) |
| C(16) | 1.2129(8) | 0.1818(4) | 0.7745(4) | 3.5(2) |
| C(17) | 1.1486(9) | 0.1729(4) | 0.8374(4) | 4.1(2) |
| C(18) | 1.181(1) | 0.2199(4) | 0.9046(4) | 5.0(2) |
| C(19) | 1.344(1) | 0.2281(5) | 0.9273(5) | 7.2(3) |
| C(20) | 1.112(1) | 0.2874(5) | 0.8828(6) | 7.5(3) |
| C(21) | 1.117(1) | 0.1946(5) | 0.9703(5) | 6.8(3) |
| C(111) | 1.2156(7) | -0.0062(4) | 0.6647(4) | 3.2(1) * |
| C(112) | 1.3618(8) | -0.0224(4) | 0.6732(4) | 4.3(2) * |
| C(113) | 1.4257(9) | -0.0377(4) | 0.6133(5) | 4.8(2) * |
| C(114) | 1.3526(9) | -0.0382(5) | 0.5447(5) | 5.1(2) * |
| C(115) | 1.210(1) | -0.0238(5) | 0.5350(5) | 5.9(2) * |
| C(116) | 1.1422(9) | -0.0079(4) | 0.5948(5) | 4.8(2) * |
| C(117) | 1.0871(8) | -0.0665(4) | 0.7767(4) | 3.6(2) * |
| C(118) | 1.0822(9) | -0.0772(4) | 0.8502(5) | 4.4(2) * |
| C(119) | 1.035(1) | -0.1383(5) | 0.8736(6) | 6.1(2) * |
| C(120) | 0.993(1) | -0.1864(5) | 0.8231(5) | 6.0(2) * |
| C(121) | 1.001(1) | -0.1779(5) | 0.7520(5) | 5.5(2) * |
| C(122) | 1.0487(9) | -0.1177(4) | 0.7271(5) | 4.6(2) * |
| C(211) | 1.1877(8) | 0.1643(4) | 0.6115(4) | 3.5(2) * |
| C(212) | 1.1064(9) | 0.1596(4) | 0.5435(5) | 4.8(2) * |
| C(213) | 1.170(1) | 0.1500(5) | 0.4819(5) | 5.7(2) * |
| C(214) | 1.317(1) | 0.1447(5) | 0.4885(5) | 5.7(2) * |
| C(215) | 1.3972(9) | 0.1482(5) | 0.5558(5) | 4.9(2) * |
| C(216) | 1.3350(8) | 0.1574(4) | 0.6184(4) | 4.1(2) * |
| C(217) | 1.0322(8) | 0.2678(4) | 0.6695(4) | 3.6(2) * |
| C(218) | 0.926(1) | 0.2943(5) | 0.7050(5) | 5.4(2) * |
| C(219) | 0.880(1) | 0.3591(5) | 0.6922(5) | 5.9(2) * |
| C(220) | 0.940(1) | 0.3971(5) | 0.6437(5) | 6.0(2) * |
| C(221) | 1.042(1) | 0.3724(5) | 0.6085(5) | 6.1(2) * |
| C(222) | 1.0918(9) | 0.3071(5) | 0.6205(5) | 5.2(2) * |

V, assignable to the $0/1^-$ and $1^-/2^-$ redox couples, as shown by the CV in Fig. 2. On the basis of the usual electrochemical criteria for reversibility, the $0/1^-$ re-

dox couple may be considered as a reversible, one-electron transfer [20]; however, the $1^-/2^-$ redox couple is best viewed as a quasi-reversible one-electron process

Table 3 (continued)

| Atom | x | y | z | B, (Å ²) |
|--|-----------|------------|-----------|----------------------|
| Co ₂ (CO) ₄ [η ² :η ² :η ¹ :η ¹ -PhC=C(Me)PPh ₂ C=C(PPh ₂)C(O)OC(O)] (3z) | | | | |
| Co(1) | 0.5738(2) | 0.2999(1) | 0.3489(1) | 3.47(4) |
| Co(2) | 0.8148(2) | 0.2363(1) | 0.3344(1) | 3.33(4) |
| P(1) | 0.5836(3) | 0.3025(3) | 0.2189(2) | 3.47(7) |
| P(2) | 0.5944(3) | 0.0441(3) | 0.2892(2) | 3.13(7) |
| O(1) | 0.636(1) | 0.5128(8) | 0.4559(6) | 7.5(3) |
| O(2) | 0.274(1) | 0.3202(9) | 0.3393(7) | 8.1(3) |
| O(3) | 1.0806(9) | 0.1374(8) | 0.3733(7) | 6.9(3) |
| O(4) | 0.956(1) | 0.4542(8) | 0.3963(8) | 8.4(3) |
| O(12) | 0.8448(9) | 0.2591(8) | 0.1105(5) | 5.3(2) |
| O(13) | 0.8750(8) | 0.0991(7) | 0.1564(5) | 4.4(2) |
| O(14) | 0.8417(9) | -0.0568(7) | 0.2068(5) | 4.7(2) |
| C(1) | 0.617(2) | 0.428(1) | 0.4114(8) | 5.2(3) |
| C(2) | 0.390(1) | 0.314(1) | 0.3427(8) | 4.8(3) |
| C(3) | 0.975(1) | 0.176(1) | 0.3589(8) | 4.0(3) |
| C(4) | 0.897(2) | 0.370(1) | 0.3702(8) | 5.2(4) |
| C(11) | 0.719(1) | 0.2096(9) | 0.2105(6) | 2.9(2) * |
| C(12) | 0.814(1) | 0.201(1) | 0.1552(7) | 3.9(3) * |
| C(14) | 0.818(1) | 0.037(1) | 0.2052(7) | 3.8(3) * |
| C(15) | 0.723(1) | 0.1071(9) | 0.2463(7) | 3.2(2) * |
| C(16) | 0.569(1) | 0.1407(9) | 0.3718(7) | 3.4(2) * |
| C(17) | 0.698(1) | 0.2057(9) | 0.4143(7) | 3.5(2) * |
| C(18) | 0.755(1) | 0.217(1) | 0.5045(7) | 3.7(2) * |
| C(19) | 0.816(1) | 0.315(1) | 0.5542(9) | 5.4(3) * |
| C(20) | 0.874(2) | 0.320(1) | 0.638(1) | 7.0(4) * |
| C(21) | 0.873(2) | 0.229(1) | 0.6752(9) | 6.3(4) * |
| C(22) | 0.816(1) | 0.132(1) | 0.6291(8) | 5.2(3) * |
| C(23) | 0.760(1) | 0.126(1) | 0.5438(7) | 4.1(3) * |
| C(111) | 0.434(1) | 0.251(1) | 0.1327(7) | 4.0(3) * |
| C(112) | 0.445(1) | 0.168(1) | 0.0700(8) | 4.2(3) * |
| C(113) | 0.330(2) | 0.128(1) | 0.0053(9) | 5.7(3) * |
| C(114) | 0.204(2) | 0.173(1) | 0.0032(9) | 6.3(4) * |
| C(115) | 0.188(2) | 0.255(1) | 0.0635(9) | 6.2(4) * |
| C(116) | 0.303(1) | 0.293(1) | 0.1310(9) | 5.5(3) * |
| C(117) | 0.638(1) | 0.430(1) | 0.1863(7) | 3.9(3) * |
| C(118) | 0.623(2) | 0.438(1) | 0.1027(9) | 6.2(4) * |
| C(119) | 0.662(2) | 0.537(1) | 0.079(1) | 7.4(4) * |
| C(120) | 0.717(2) | 0.626(1) | 0.137(1) | 6.5(4) * |
| C(121) | 0.733(2) | 0.620(1) | 0.2172(9) | 6.3(4) * |
| C(122) | 0.694(1) | 0.521(1) | 0.2416(9) | 5.4(3) * |
| C(161) | 0.463(1) | 0.103(1) | 0.4177(8) | 4.2(3) * |
| C(211) | 0.660(1) | -0.074(1) | 0.3341(7) | 3.6(2) * |
| C(212) | 0.800(1) | -0.077(1) | 0.3770(8) | 4.3(3) * |
| C(213) | 0.841(1) | -0.160(1) | 0.4213(8) | 5.2(3) * |
| C(214) | 0.743(1) | -0.241(1) | 0.4249(9) | 5.5(3) * |
| C(215) | 0.607(1) | -0.241(1) | 0.3841(8) | 4.9(3) * |
| C(216) | 0.565(1) | -0.158(1) | 0.3383(8) | 4.6(3) * |
| C(217) | 0.440(1) | -0.0090(9) | 0.2107(7) | 3.1(2) * |
| C(218) | 0.454(1) | -0.098(1) | 0.1527(8) | 4.5(3) * |
| C(219) | 0.338(2) | -0.141(1) | 0.0903(9) | 5.5(3) * |
| C(220) | 0.209(2) | -0.097(1) | 0.0864(9) | 6.4(4) * |
| C(221) | 0.194(1) | -0.010(1) | 0.1432(8) | 5.2(3) * |
| C(222) | 0.310(1) | 0.035(1) | 0.2067(7) | 3.8(3) * |
| C(1) | 0.322(2) | 0.603(1) | 0.164(1) | 15.7(5) * |
| C(2) | 0.075(2) | 0.562(2) | 0.100(1) | 20.5(8) * |

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$.

given its diminished current ratio ($I_{p^a}/I_{p^c} \approx 0.8$ at 0.1 V s^{-1}) and its involvement in the EC scheme that affords the unknown electroactive species at $E_{p^a} = -0.53$ V. Switching the CV potential short of the $1^-/2^-$ redox

couple (-1.20 V) does not produce this unknown redox species. Both reductions in **3z** exhibit ΔE_p values on the order of 100 mV and are larger than the 80 mV obtained from internally added Cp_2^*Fe . These data sug-

Table 4
Selected bond distances (Å) and angles (deg) in compounds **1z**, **2b**, **2z**, and **3z**^a

| | | | |
|--|-----------|-------------------|-----------|
| Co₂(CO)₄[μ-η^2:η^2:η^1:η^1-PhC=C(H)PPh₂$\overline{C=C(PPh_2)C(O)OC(O)}$] (1z) | | | |
| <i>Bond distances</i> | | | |
| Co(1)–Co(2) | 2.549(1) | Co(1)–P(1) | 2.204(2) |
| Co(1)–C(21) | 2.015(8) | Co(1)–C(22) | 1.899(7) |
| Co(2)–C(11) | 2.056(7) | Co(2)–C(15) | 2.016(7) |
| Co(2)–C(22) | 2.005(7) | C(11)–C(15) | 1.43(1) |
| C(21)–C(22) | 1.43(1) | | |
| <i>Bond angles</i> | | | |
| Co(2)–Co(1)–P(1) | 72.87(6) | Co(2)–Co(1)–C(21) | 75.7(2) |
| Co(2)–Co(1)–C(22) | 51.1(2) | P(1)–Co(1)–C(21) | 112.1(2) |
| P(1)–Co(1)–C(22) | 120.5(2) | C(21)–Co(1)–C(22) | 42.6(3) |
| C(11)–Co(2)–C(15) | 41.1(3) | C(11)–Co(2)–C(22) | 118.4(3) |
| C(15)–Co(2)–C(22) | 96.4(3) | C(15)–P(2)–C(21) | 105.9(4) |
| Co₂(CO)₄(bma)(μ-HC≡C^tBu) (bridging isomer) (2b) | | | |
| <i>Bond distances</i> | | | |
| Co(1)–Co(2) | 2.466(1) | Co(1)–P(1) | 2.220(2) |
| Co(1)–C(16) | 1.960(6) | Co(1)–C(17) | 1.965(6) |
| Co(2)–P(2) | 2.215(2) | Co(2)–C(16) | 1.965(6) |
| Co(2)–C(17) | 1.969(6) | C(11)–C(15) | 1.333(8) |
| C(16)–C(17) | 1.349(9) | C(17)–C(18) | 1.509(9) |
| <i>Bond angles</i> | | | |
| Co(2)–Co(1)–P(1) | 105.61(5) | Co(1)–Co(2)–P(2) | 102.93(6) |
| Co(1)–P(1)–C(11) | 116.9(2) | Co(2)–P(2)–C(15) | 116.3(2) |
| P(1)–C(11)–C(15) | 127.5(4) | P(2)–C(15)–C(11) | 127.2(4) |
| C(16)–C(17)–C(18) | 140.7(5) | | |
| Co₂(CO)₄[μ-η^2:η^2:η^1:η^1-^tBuC=C(H)PPh₂$\overline{C=C(PPh_2)C(O)OC(O)}$] (2z) | | | |
| <i>Bond distances</i> | | | |
| Co(1)–Co(2) | 2.564(1) | Co(1)–P(1) | 2.189(2) |
| Co(1)–C(16) | 2.021(7) | Co(1)–C(17) | 1.920(8) |
| Co(2)–C(11) | 2.078(7) | Co(2)–C(15) | 2.036(7) |
| Co(2)–C(17) | 2.026(8) | C(11)–C(15) | 1.44(1) |
| C(16)–C(17) | 1.40(1) | | |
| <i>Bond angles</i> | | | |
| Co(2)–Co(1)–P(1) | 74.29(6) | Co(2)–Co(1)–C(16) | 73.8(2) |
| Co(2)–Co(1)–C(17) | 51.3(2) | P(1)–Co(1)–C(16) | 109.3(2) |
| P(1)–Co(1)–C(17) | 121.1(2) | C(16)–Co(1)–C(17) | 41.5(3) |
| Co(1)–Co(2)–C(17) | 47.7(2) | C(11)–Co(2)–C(15) | 40.9(3) |
| C(11)–Co(2)–C(17) | 116.6(3) | C(15)–Co(2)–C(17) | 96.1(3) |
| Co₂(CO)₄[μ-η^2:η^2:η^1:η^1-PhC=C(Me)PPh₂$\overline{C=C(PPh_2)C(O)OC(O)}$] (3z) | | | |
| <i>Bond distances</i> | | | |
| Co(1)–Co(2) | 2.548(2) | Co(1)–P(1) | 2.202(4) |
| Co(1)–C(16) | 2.05(1) | Co(1)–C(17) | 1.96(1) |
| Co(2)–C(11) | 2.05(1) | Co(2)–C(15) | 2.03(1) |
| Co(2)–C(17) | 2.01(1) | P(2)–C(16) | 1.75(1) |
| C(11)–C(15) | 1.47(2) | C(16)–C(17) | 1.44(1) |
| C(16)–C(161) | 1.51(2) | | |
| <i>Bond angles</i> | | | |
| Co(2)–Co(1)–P(1) | 73.2(1) | Co(2)–Co(1)–C(16) | 76.0(3) |
| Co(2)–Co(1)–C(17) | 50.8(4) | P(1)–Co(1)–C(16) | 110.0(3) |
| P(1)–Co(1)–C(17) | 119.1(4) | C(16)–Co(1)–C(17) | 41.9(4) |
| Co(1)–Co(2)–C(17) | 49.4(3) | C(11)–Co(2)–C(15) | 42.2(4) |
| Co(1)–C(16)–C(161) | 119.0(8) | P(2)–C(16)–C(161) | 115.1(8) |
| C(17)–C(16)–C(161) | 122(1) | C(16)–C(17)–C(18) | 123(1) |

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

gest that the rate of heterogeneous electron transfer k_{het} is slow in **3z** in comparison with the one-electron standard Cp_2^+Fe . Not shown in Fig. 2 is the irreversible oxidation at $E_p = 0.76$ V, which remained irreversible at scan rates up to 1 V s^{-1} .

We also investigated the use of CH_2Cl_2 and MeCN as CV solvents and found only a single, broad two-electron reduction having a ΔE_p value in excess of 220 mV (not shown) at all scan rates examined. The oxidative wave in **3z** still remained irreversible and was not

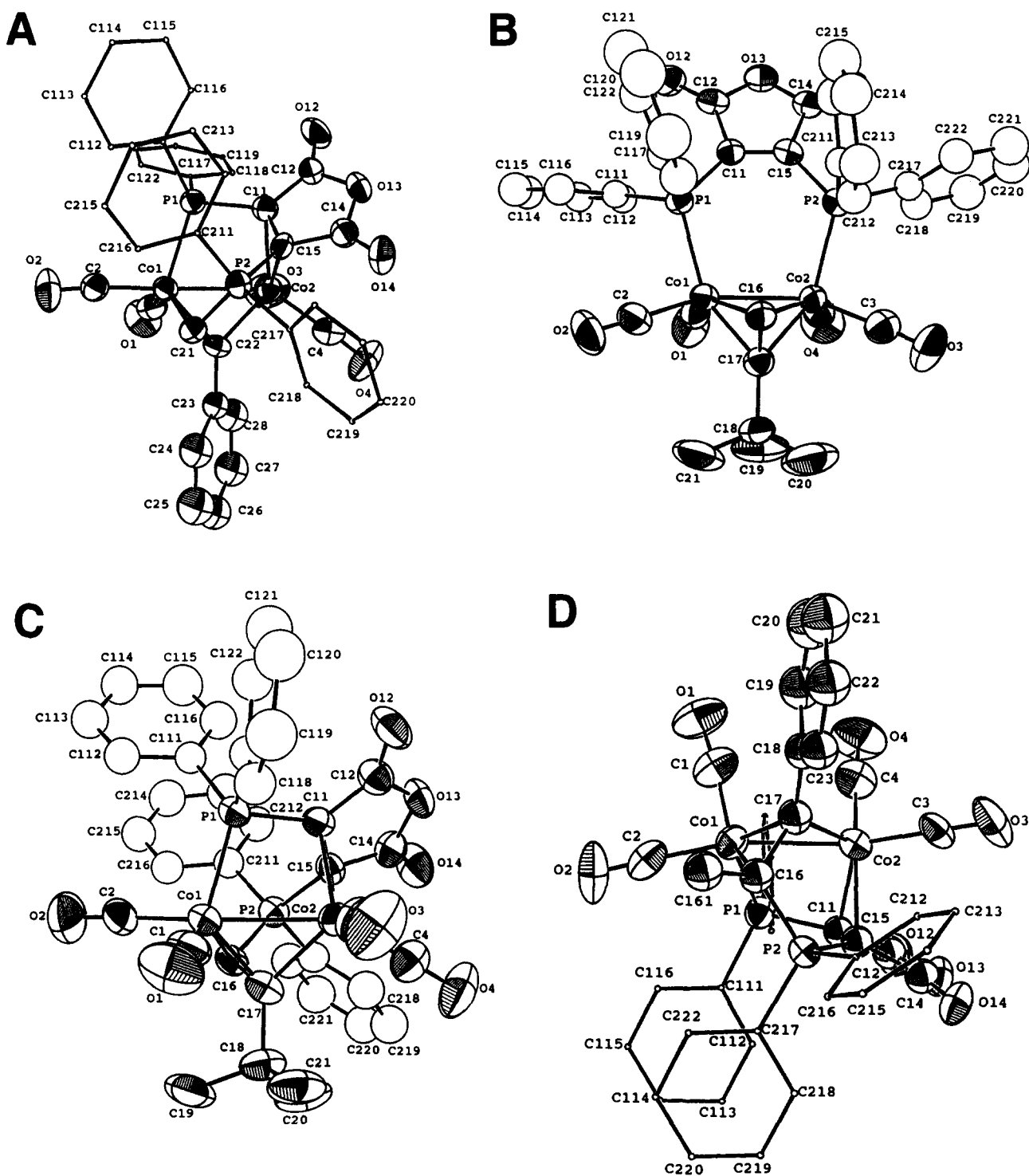


Fig. 1. ORTEP diagrams of the non-hydrogen atoms of (A) $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-PhC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ (**1z**), (B) $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C}^1\text{Bu})$ (bridging isomer) (**2b**), (C) $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-}^1\text{BuC=C(H)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ (**2z**) and (D) $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-PhC=C(Me)PPh}_2\text{C=C(PPh}_2\text{)C(O)OC(O)}]$ (**3z**) showing the thermal ellipsoids at the 50% probability level.

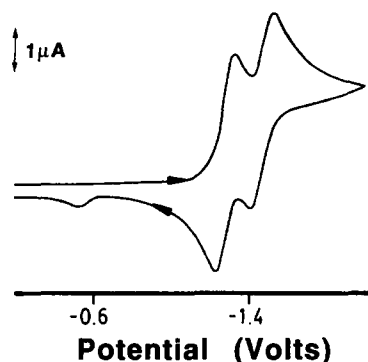


Fig. 2. Cathodic scan cyclic voltammogram of **3z** (ca. 10^{-3} M) in THF containing 0.2 M TBAP at 0.1 V s^{-1} at 298 K.

explored further. The loss of peak resolution and the observed peak broadening in the reduction most likely stems from a slow charge transfer in the slightly more polar solvents that cause the merging of the reduction waves [21].

The reductive electrochemistry reported for **3z** indicates that complexation of the bma ligand helps to stabilize the added electron in the $0/1^-$ redox couple by using a low-lying π^* orbital, and this stands in contrast to the electrochemical behavior of the parent alkyne $\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})$ and its phosphine-substituted derivatives, which all exhibit a chemically irreversible reduction process involving the addition of the added electron to a σ Co–Co antibonding orbital [22]. The reduction of several mononuclear bma-substituted compounds to the corresponding 19-electron complexes has been discussed in terms of an $18 + \delta$ designation, which indicates that the odd electron is almost exclusively associated with the π^* orbital of the bma ligand [8,23,24]. Experimental data (EPR and X-ray) have unambiguously demonstrated that such compounds are not bona fide 19-electron complexes because electron accession does not lead to population of a high-energy

metal–ligand antibonding orbital [8]. However, a prediction concerning the nature of the reduction product in **3z** \cdot^- is not immediately clear. Since the reduction potential ($0/1^-$ couple) for free bma and the known $18 + \delta$ bma complexes occurs at potentials below -1.0 V, our observed potential data for the hydrocarbyl **3z** suggests that the site of electron accession in the radical anion is not entirely confined to the bma ligand. To our knowledge no electrochemical data have been reported for a bma compound having a coordinated maleic anhydride π bond.

2.4. Extended Hückel calculations on $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-HC}=\text{C(H)PH}_2\text{C}=\text{C(PH}_2\text{)C(O)OC(O)}]$

The orbital composition of the HOMO and LUMO of the model hydrocarbyl compound $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-HC}=\text{C(H)PH}_2\text{C}=\text{C(PH}_2\text{)C(O)OC(O)}]$ was examined by extended Hückel molecular orbital calculations. The calculations were carried out using the crystallographic data for **3z**, and for simplicity purposes all of the phenyl groups were replaced by hydrogens. Fig. 3 shows the three-dimensional CACAO drawings of the two relevant orbitals [25].

The HOMO of the hydrocarbyl complex is found to have an energy of -11.53 eV and contains major contributions from the two cobalt centers (30%), the hydrocarbyl moiety (19%), and the bma ligand (17%), in addition to minor Co–CO bonding interactions. The Co–Co bond present is derived from the overlap of d_{yz} orbitals, which in the case of the phosphine-substituted cobalt center has been hybridized by added p_z character similar to that found in other binuclear systems [26]. More extensive hybridization (p_y , p_z , $d_{x^2-y^2}$, and d_{xz} character) is found at the cobalt center bearing the maleic anhydride ring, which in turn facilitates the bonding interactions between this cobalt center and the

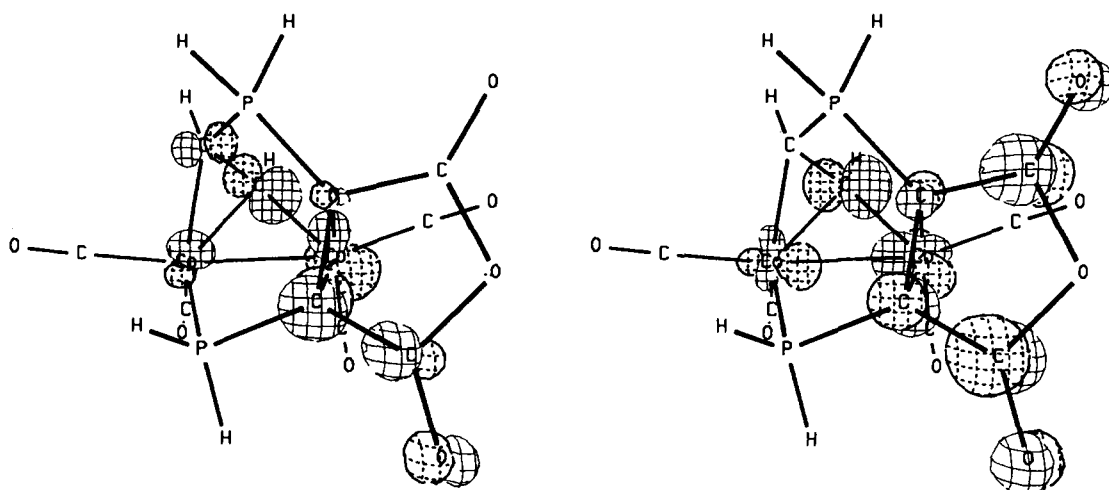


Fig. 3. CACAO drawings of the HOMO (left) and LUMO (right) of $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-HC}=\text{C(H)PH}_2\text{C}=\text{C(PH}_2\text{)C(O)OC(O)}]$.

hydrocarbyl moiety and maleic anhydride ring. The orbital contribution of the bma ligand to the HOMO derives from the partial utilization of the π^* orbital of an isolated bma ligand (vide infra). This particular orbital bears resemblance to ψ_4 of maleic anhydride and related six- π -electron systems [27].

The LUMO lies at relatively high energy (-9.96 eV) and is similar to the HOMO in that it is composed of major contributions from the cobalt centers and the hydrocarbyl and bma ligands. The Co–Co bond (27%) is clearly antibonding and results from extensive hybridization of the $d_{x^2-y^2}$ orbitals, and the non-phosphine-substituted hydrocarbyl carbon (17%) acts as a bonding bridge between these two metal centers. The full participation of the bma π^* orbital (36%) and its antibonding overlap with the cobalt center are clearly seen in the CACAO drawing. The minor Co–CO antibonding contributions to the LUMO are not shown.

Whereas the LUMO in the bridging and chelating bma isomers of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ has been shown to reside exclusively at the bma ligand [6], the LUMO in the model hydrocarbyl compound presented here is much more complex and contains added metal and ligand character. Accordingly, the radical anion $3z \cdot^-$ produced upon one-electron reduction should not be considered as a $36 + \delta$ compound but rather a 37-electron binuclear compound [24]. That this description is reasonable is confirmed by the difference in the $0/1^-$ reduction potentials of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CPh})$ (both isomers) and the hydrocarbyl compounds **1z**, **2z**, and **3z** (vide supra). The reduction potential ($0/1^-$) of the known $36 + \delta$ compounds is close to that of the free bma ligand while the hydrocarbyl compounds reported here all display ca. -0.7 V shift to more negative potential. So, despite the fact that the bma π^* orbital is not the sole repository of added electron density in $3z \cdot^-$, the stabilization that this ligand confers on the binuclear frame is still significant in comparison with other binuclear compounds of this genre and suggests that the redox tuning of these systems may be controlled by simply altering the coordination mode of the bma ligand. The exploitation of this premise is currently under investigation.

3. Experimental section

3.1. General procedures

The phenylacetylene, *t*-butylacetylene, 3-phenyl-1-propyne, and 2,3-dichloromaleic anhydride were all purchased from Aldrich Chemical Co. and used directly without purification. The $\text{Co}_2(\text{CO})_8$ used in the preparation of the $\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})$ compounds was obtained from Strem Chemicals, Inc. THF was distilled from Na–benzophenone, while CH_2Cl_2 , CDCl_3 , and

1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ were all distilled from P_2O_5 . All purified solvents were transferred to storage vessels equipped with Teflon stopcocks using Schlenk techniques [28]. The TBAP (*caution*: strong oxidant) was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate–petroleum ether, after which it was dried under vacuum for at least 48 h. Microanalyses were performed by Atlantic Microlab, Norcross, GA.

All infrared spectra were recorded on a Nicolet 20SXB FT-IR in 0.1 mm NaCl cells. The ^{13}C and ^{31}P NMR spectra were recorded on a Varian 300-VXR spectrometer at 75 and 121 MHz respectively, while the ^1H NMR spectra were recorded on a Varian 200 Gemini-200 spectrometer at 200 MHz. The ^{31}P NMR data were referenced to external H_3PO_4 (85%), taken to have $\delta = 0$, with positive chemical shifts representing resonances that are to low field of the external standard.

3.2. Synthesis of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{CPh})$ (**1c**)

To a Schlenk tube containing 0.1 g (0.26 mmol) of $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CH})$ 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 was then stirred for 1 h and examined by TLC analysis, which revealed the complete consumption of $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CH})$ and the formation of **1c** (chelating isomer). After solvent removal, **1c** 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 **1c**. Anal. Calc. (found) for $\text{C}_{40}\text{H}_{26}\text{Co}_2\text{O}_7\text{P}_2 \cdot 1/3\text{CH}_2\text{Cl}_2$: C, 58.52 (58.59); H, 3.42 (3.25)%.

3.3. Synthesis of $\text{Co}_2(\text{CO})_4[\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-PhC}=\text{C(H)PPh}_2\bar{\text{C}}=\text{C(PPh}_2)\text{C(O)OC(O)}]$ (**1z**)

To a Schlenk tube containing 0.2 g (0.25 mmol) of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-PhC}\equiv\text{CH})$ (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 **1z** in greater than 90% yield. After solvent removal, **1z** was then chromatographed over silica gel using CH_2Cl_2 as the eluant. The microanalytical sample and single-crystals of **1z** suitable for X-ray diffraction analysis were obtained from CH_2Cl_2 –heptane (1:1). Yield: 0.30 g (70%) of black **1z**. Anal. Calc. (found) for $\text{C}_{40}\text{H}_{26}\text{Co}_2\text{O}_7\text{P}_2 \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 57.84 (57.87); H, 3.24 (3.26)%.

3.4. Synthesis of $\text{Co}_2(\text{CO})_4(\text{bma})(\mu\text{-HC}\equiv\text{C}^i\text{Bu})$ (**2c**)

Compound **2c** was prepared in identical fashion as described for **1c**. The desired product was isolated by chromatography over silica gel at -78 °C using CH_2Cl_2 –petroleum ether (3:1) as the eluant, followed by recrystallization from CH_2Cl_2 –pentane, to afford

0.12 g (57%) of black **2c**. Anal. Calc. (found) for $C_{38}H_{30}Co_2O_7P_2$: C, 58.62 (58.58); H, 3.88 (3.88)%.

3.5. Synthesis of $Co_2(CO)_4(bma)(\mu-HC\equiv C'Bu)$ (**2b**)

To a Schlenk tube containing 0.10 g (0.13 mmol) of **2c** was added 50 ml of 1,2-dichloroethane under argon. The vessel was sealed and then heated at 45 °C for over 30 h. Upon cooling, the solution was examined by IR and TLC analyses, which showed the major product to be that of **2b**, in addition to a small amount of **2c**. The bridging isomer was isolated by chromatography over silica gel at –78 °C using CH_2Cl_2 as the eluant. The microanalytical sample and single crystals suitable for X-ray diffraction analysis were obtained from CH_2Cl_2 –pentane. Yield: 0.060 g (60%) of black **2b**. Anal. Calc. (found) for $C_{38}H_{30}Co_2O_7P_2$: C, 58.62 (58.67); H, 3.88 (3.92)%.

3.6. Synthesis of $Co_2(CO)_4[\mu-\eta^2:\eta^2:\eta^1:\eta^1-\text{'BuC}=\text{C(H)PPh}_2\bar{C}=\text{C(PPh}_2\text{)C(O)OC(O)}]$ (**2z**)

The hydrocarbyl compound **2z** was prepared in a manner identical with that employed for **1z**, starting from 0.1 g of **2b**. The final product was purified by column chromatography over silica gel with CH_2Cl_2 , and the microanalytical sample and single crystals suitable for X-ray diffraction analysis were obtained from CH_2Cl_2 –pentane (1:1). Yield: 0.060 g (60%) of black **2z**. Anal. Calc. (found) for $C_{38}H_{30}Co_2O_7P_2$: C, 58.62 (58.51); H, 3.88 (3.91)%.

3.7. Synthesis of $Co_2(CO)_4(bma)(\mu-MeC\equiv CPh)$ (**3c**)

The chelating isomer was prepared in identical fashion as described for **1c**. The product **3c** was isolated by chromatography (vide supra) and recrystallized from CH_2Cl_2 –pentane (1:1), which afforded black crystals of **3c**. Yield: 0.070 g (70%). Anal. Calc. (found) for $C_{41}H_{28}Co_2O_7P_2$: C, 60.61 (60.36); H, 3.47 (3.61)%.

3.8. Synthesis of $Co_2(CO)_4(bma)(\mu-MeC\equiv CPh)$ (**3b**)

Thermolysis of 0.1 g of **3c** in 100 ml of 1,2-dichloroethane overnight led to an equilibrium mixture of **3c** and **3b**. TLC analysis showed two very close moving spots in CH_2Cl_2 –petroleum ether (1:1) (R_f difference less than 0.1). None of the solvent systems examined provided sufficient separation of these two isomers, and as a result we could not isolate **3b** without contamination by **3c**. All attempts at recrystallization also failed to produce pure samples of **3b**. Accordingly, **3b** was characterized in situ from an isomeric mixture of **3c** and **3b**.

3.9. Synthesis of $Co_2(CO)_4[\mu-\eta^2:\eta^2:\eta^1:\eta^1-PhC=\text{C(Me)PPh}_2\bar{C}=\text{C(PPh}_2\text{)C(O)OC(O)}]$ (**3z**)

Thermolysis of a 0.1 g sample containing **3c** and **3b** in refluxing 1,2-dichloroethane for 1.0 h revealed, after

cooling, the absence of starting materials and the presence of the desired hydrocarbyl compound by TLC analysis. **3z** was purified by column chromatography over silica gel using CH_2Cl_2 , after which recrystallization from toluene–pentane (1:1) afforded the microanalytical sample. Single crystals of **3z** suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 solution containing **3z** that had been layered with heptane. Yield: 0.065 g (65%) of black **3z**. Anal. Calc. (found) for $C_{41}H_{28}Co_2O_7P_2$: C, 60.61 (61.04); H, 3.47 (3.80)%.

3.10. X-ray crystallography

All data were collected on an Enraf–Nonius CAD-4 diffractometer using the θ – 2θ scan technique, Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. Standard procedures for the data collection have been previously described [29]. Pertinent details are given in Table 2. Data were corrected for Lorentz and polarization effects, as well as for absorption (DIFABS) [30]. The structures were solved by direct methods (SIR (**1z** and **2z**)) [31], MULTAN (**3z**) [32], and SHELXS-86 (**2b**) [33] and the model refined by using full-matrix least squares techniques. The treatment of the thermal parameters was based on the number of observed data, where anisotropic parameters were incorporated for the Co, P, O, and the carbonyl carbons in **3z**, and all of the non-hydrogen, non-phenyl carbons in the other three structures. Hydrogen atoms were located on the difference maps, and then included in the model in idealized positions ($U(H) = 1.3 B_{eq}(C)$). All computations other than those specified were performed by using MolEN [34]. Scattering factors were taken from the usual sources [35].

3.11. Electrochemical studies

Cyclic voltammograms were obtained with a PAR Model 273 potentiostat–galvanostat, equipped with positive feedback circuitry to compensate for iR drop. The air-tight cyclic voltammetry cell was based on a three-electrode design, and all CV experiments employed a platinum disk as the working and auxiliary electrode. The reference electrode in these experiments consisted of a silver wire quasi-reference electrode, with all potential data reported relative to the formal potential of the $Cp_2^*Fe-Cp_2^*Fe^+$ (internally added) redox couple, taken to have $E_{1/2} = -0.20 \text{ V}$ [36].

3.12. Molecular orbital calculations

The extended Hückel calculations reported here were carried out with the original program developed by Hoffmann [37], as modified by Mealli and Proserpio [25]. The input Z-matrix for $Co_2(CO)_4[\mu-\eta^2:\eta^2:\eta^1:\eta^1-HC=\text{C(H)PPh}_2\bar{C}=\text{C(PH}_2\text{)C(O)OC(O)}]$ was constructed by replacing all of the phenyl groups on the bma and

alkenyl ligands and the methyl group on the alkenyl ligand with hydrogen groups using the PC modelling program MOBY. The C–H (1.07 Å) and P–H (1.42 Å) distances used in the extended Hückel calculations were taken from model compounds [38].

4. Supplementary material available

Textual presentations of the crystallographic experimental details and listings of crystallographic data, bond distances, bond angles, and hydrogen positional and thermal parameters for compounds **1z**, **2b**, **2z**, and **3z**.

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