ETC and Thermal Ligand Substitution in PhCCo$_3$(CO)$_9$ with 2,3-Bis(diphenylphosphino)-N-phenylmaleimide (bppm).

X-Ray Diffraction Structure of Co$_3$(CO)$_6$[µ$_2$-η$^1$-C(Ph)C≡C(PPh$_2$)(O)NPhC(O)](µ$_2$-PPh$_2$)

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The reactivity of the bidentate ligand 2,3-bis(diphenylphosphino)-N-phenylmaleimide (bppm) with the tetrahedrane cluster PhCCo$_3$(CO)$_9$ under thermolysis and ETC conditions has been studied and found to ultimately give Co$_3$(CO)$_6$[µ$_2$-η$^2$-C(Ph)C≡C(PPh$_2$)(O)NPhC(O)](µ$_2$-PPh$_2$) as the final product. The intermediate cluster compound PhCCo$_3$(CO)$_7$(bppm), which was observed by IR and $^{31}$P NMR spectroscopies, readily and rapidly transforms into the product cluster under the reaction conditions. The solid-state structure of Co$_3$(CO)$_6$[µ$_2$-η$^2$-C(Ph)C≡C(PPh$_2$)(O)NPhC(O)](µ$_2$-PPh$_2$) was unequivocally determined by X-ray crystallography.

INTRODUCTION

For the last several years our research interests have centered on the coordination and redox chemistry of polynuclear clusters containing an ancillary diphosphine ligand [1]. While many diphosphine ligands exist and have been investigated by us for their ligand substitution chemistry, we have had a special interest in the reactivity exhibited by the redox-active ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) [2] and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) [3]. For example, we have shown that when these particular ligands are coordinated to a transition-metal cluster compound, facile P-C bond cleavage and cluster activation are readily observed under mild conditions, as depicted in Eq. 1 for the clusters PhCCo$_3$(CO)$_7$(P-P) (where P-P = bma, bpcd) [2a, 3e].

Wishing to extend our ligand reactivity studies that have previously utilized the diphosphine ligands bma and bpcd with the related maleimide derivative 2,3-bis(diphenylphosphino)-N-phenylmaleimide (bppm), we
have explored the substitution chemistry of PhCCO\(_3\)(CO)\(_9\) with bppm. The structures of these three diphosphine ligands are shown below. While the ligand bppm has been used as an ancillary ligand in the preparation of mononuclear metal compounds [4], our study represents the first report of a reaction between bppm and a polynuclear metal cluster compound. Herein, we report our data on the coordination of bppm to the tricobalt cluster PhCCO\(_3\)(CO)\(_9\) to initially give PhCCO\(_3\)(CO)\(_7\)(bppm), followed by the transformation to Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)). Both products have been characterized in solution by IR and \(^{31}\)P spectroscopies, and the molecular structure of the latter cluster has been determined by X-ray analysis. Structural comparisons of Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)) with the bma- and bpcd-substituted analogs are presented.

**EXPERIMENTAL SECTION**

**General**

The starting cluster PhCCO\(_3\)(CO)\(_9\) was prepared according to the procedure of Seyferth [5] and the bppm ligand was synthesized from 2,3-dichloro-N-phenylmaleimide [6] and Ph\(_2\)PSiMe\(_3\) [7]. The solvents used in the syntheses and electrochemical studies were distilled from an appropriate drying agent under argon and stored in Schlenk storage vessels equipped with Teflon stopcocks. Schlenk techniques were employed in the synthesis and handling of all air-sensitive materials [8]. The tetra-n-butylammonium perchlorate (TBAP; caution: strong oxidant) was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate/petroleum ether. The supporting electrolyte was dried under vacuum for at least 48 hr prior to use. The combustion analysis was performed by Atlantic Microlab (Norcross, GA).

Infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1-mm NaCl cells, using PC control and OMNIC software, and the \(^{31}\)P NMR spectra were recorded at 121 MHz on a Varian 300-VXR spectrometer. \(^{31}\)P chemical shifts are referenced relative to external H\(_3\)PO\(_4\) (85%), taken to have \(\delta = 0\).

**Experimental Section**

**General**

The starting cluster PhCCO\(_3\)(CO)\(_9\) was prepared according to the procedure of Seyferth [5] and the bppm ligand was synthesized from 2,3-dichloro-N-phenylmaleimide [6] and Ph\(_2\)PSiMe\(_3\) [7]. The solvents used in the syntheses and electrochemical studies were distilled from an appropriate drying agent under argon and stored in Schlenk storage vessels equipped with Teflon stopcocks. Schlenk techniques were employed in the synthesis and handling of all air-sensitive materials [8]. The tetra-n-butylammonium perchlorate (TBAP; caution: strong oxidant) was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate/petroleum ether. The supporting electrolyte was dried under vacuum for at least 48 hr prior to use. The combustion analysis was performed by Atlantic Microlab (Norcross, GA).

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**Thermolysis of PhCCO\(_3\)(CO)\(_9\) with bppm**

To 0.52 g (1.00 mmol) of PhCCO\(_3\)(CO)\(_9\) and 0.54 g (1.00 mmol) of bppm in a Schlenk tube was added 20 mL of toluene under argon flush. The reaction solution was then stirred at 50 °C for 3 hr, after which time the solution was allowed to cool to room temperature. TLC analysis in petroleum ether/CH\(_2\)Cl\(_2\) (1:1) revealed the presence of two new materials that represented PhCCO\(_3\)(CO)\(_7\)(bppm) (\(R_f = 0.55\)) and Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)) (\(R_f = 0.35\)), along with unreacted PhCCO\(_3\)(CO)\(_9\) and bppm. Both new clusters were isolated by chromatography over silica gel using petroleum ether/CH\(_2\)Cl\(_2\) (a 4:10 mixture for the former cluster and a 6:10 mixture for the latter cluster) as the eluant. The latter cluster product was recrystallized from a mixture of hexane/CH\(_2\)Cl\(_2\). Yield of PhCCO\(_3\)(CO)\(_7\)(bppm): 0.21 g (21%). IR (CH\(_2\)Cl\(_2\); v(CO)) 2063 (vs), 2011 (vs), 1780 (vv, maleimide CO), 1720 (m, maleimide CO) cm\(^{-1}\). \(^{31}\)P NMR (CH\(_2\)Cl\(_2\), internal DCl) \(\delta\) 38.85 (bridging isomer, 85%), 58.34 and 62.83 (chelating isomer, 15%). Yield of Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)): 0.25 g (25%). IR (CH\(_2\)Cl\(_2\); v(CO)) 2057 (ms), 2035 (vs), 2020 (s), 1931 (m), 1741 (m, maleimide CO), 1697 (s, maleimide CO) cm\(^{-1}\). \(^{31}\)P NMR (CH\(_2\)Cl\(_2\), internal DCl): \(\delta\) 18.07 (s, PPh\(_2\) phosphine), 191.31 (s, PPh\(_2\) phosphido). Anal. Cald (found) for C\(_8\)H\(_8\)O\(_3\)N\(_6\)N\(_2\): C, 58.53 (58.27); H, 5.36 (5.43).

**ETC Reaction of PhCCO\(_3\)(CO)\(_9\) with bppm**

To 0.12 g (0.23 mmol) of PhCCO\(_3\)(CO)\(_9\) and 0.13 g (0.24 mmol) of bppm in 20 mL of THF at room temperature was added 3 drops of a THF solution containing sodium/benzophenone (BPK). The reaction was stirred for 1 hr and then examined by TLC analysis. At such time, the simple substitution product PhCCO\(_3\)(CO)\(_7\)(bppm) was observed as the major product (>95%). However, the conversion of PhCCO\(_3\)(CO)\(_7\)(bppm) to Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)) is noticeable as the reaction time is increased and if the chromatography is carried out at room temperature. Pure PhCCO\(_3\)(CO)\(_7\)(bppm) may be isolated by carrying out the column chromatography at low temperature (−78 °C); however, due to the facile conversion to Co\(_3\)(CO)\(_6\)[\(\mu_2\)-N\(_2\)-Ph\(_2\)-PPh\(_2\)](CO)(NPh\(_2\)C\(_O\)NPh\(_2\)C)(\(\mu_2\)-PPh\(_2\)), no attempt was made to characterize the heptacarbonyl cluster other than by IR and NMR spectroscopy.