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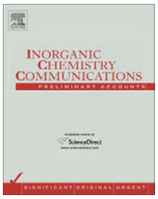

Synthesis, characterization and crystal structure of (*cis-P*,*P*′-diphenyl-1,4-diphospha-cyclohexane)molybdenum(0)tetracarbonyl

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ABSTRACT

The preparation of the novel (*cis-P*,*P*′-diphenyl-1,4-diphospha-cyclohexane)molybdenum(0)tetracarbonyl complex is described. The spectral data and X-ray structure of the title complex are reported. The results of the crystallographic work show a distorted octahedral complex around the metal center, the first of its kind reported for the *P*,*P*′-diphenyl-1,4-diphospha-cyclohexane ligand.

The use of phosphine ligands in organometallic catalysis continues to be a fertile area of study, especially with respect to structure/reactivity correlations. For example, there have recently been a number of articles published regarding the catalytic effect of various phosphine ligand bite angles on reaction yields and product distributions [1,2]. Although there exists a large body of knowledge in the literature on bidentate phosphine ligands with a single bridging carbon chain (i.e. $R_2P–C–C–PR_2$), research on cyclic bidentate phosphines with two connecting carbon chains (i.e. $RP(–C–C–)_2PR$) has recently received attention [3–7]. Such compounds are of particular interest due to the fact that the phosphorus atoms are held in a rigid steric position that could lead to distorted metal coordination geometries and different reaction chemistry than seen in their acyclic counterparts.

One cyclic bidentate phosphine ligand that shows potential for interesting metal coordination behavior is *P*,*P*′-diphenyl-1,4-diphospha-cyclohexane, (dpdpc) [8]. The *cis* isomer of this compound is especially attractive as the phosphorus atoms are held in a position where their lone pair electrons are aligned to allow for cooperative binding to a metal center. A previous study reported by Panunzi et al. on the metal coordination properties of this ligand demonstrate its versatility towards binding M(II) centers (M = Co, Ni, Pd and Pt) [9]. Fraldi et al. have shown palladium complexes of the dpdpc ligand are catalytic active towards C–C bond formation reactions [3]. Recently, work from our laboratory on dpdpc coordination reactions with Group 9 metals has identified a bridging, binuclear intermediate that can be converted to a monomeric product, illustrating the versatility of coordination modes of this ligand [10]. Further, the structurally characterized $[Cp^{*}Rh(dpdpc)Cl]PF_6$ compound shows a P–Rh–P bite angle of 71.60°, the most acute bite angle for a two-carbon bridged bidentate phosphine ligand at the time of its publication [10].

In this work we have synthesized a new metal complex of the dpdpc ligand with a Mo(0) metal center and obtained its X-ray crystal structure. Refluxing a mixture of $Mo(CO)_6$ with one equivalent of the phosphine ligand, dpdpc, in diglyme for 1 h affords the metal complex $(dpdpc)Mo(CO)_4$ as determined by $^{31}P\{^1H\}$ NMR (Scheme 1). Removal of solvent by distillation, followed by dissolution in CH_2Cl_2, filtration through celite, and removal of the solvent results in pure $Mo(dpdpc)(CO)_4$ in 15% yield [11].

The $^{31}P\{^1H\}$ NMR spectrum of $(dpdpc)Mo(CO)_4$ shows the expected downfield chemical shift from the free ligand (−27.0 ppm) to 44.3 ppm for the metal complex. The ^1H NMR spectra of the complex shows the expected peaks for the dpdpc protons, including two sets of multiplets centered at 2.47 and 2.16 ppm from the protons on the methylene backbone. The $^{13}C\{^1H\}$ NMR data shows two distinct multiplets for the carbonyl carbons at 219.5 and 208.5 ppm, attributed to the carbonyl carbons *trans*- and *cis*- to the dpdpc ligand, respectively, in addition to a four-carbon multiplet centered at 27.6 ppm from the dpdpc methylene carbon atoms [12,13].

In addition to formation of the monomeric metal complex, the presence of a bridged, binuclear intermediate can be detected in the ^{31}P NMR when monitoring the reaction progress (Scheme 1). Although the binuclear product was not isolated, a single $^{31}P\{^1H\}$ NMR resonance at 10.1 ppm is observed before the appearance of the product peak at 44.3 ppm. These resonances correspond well

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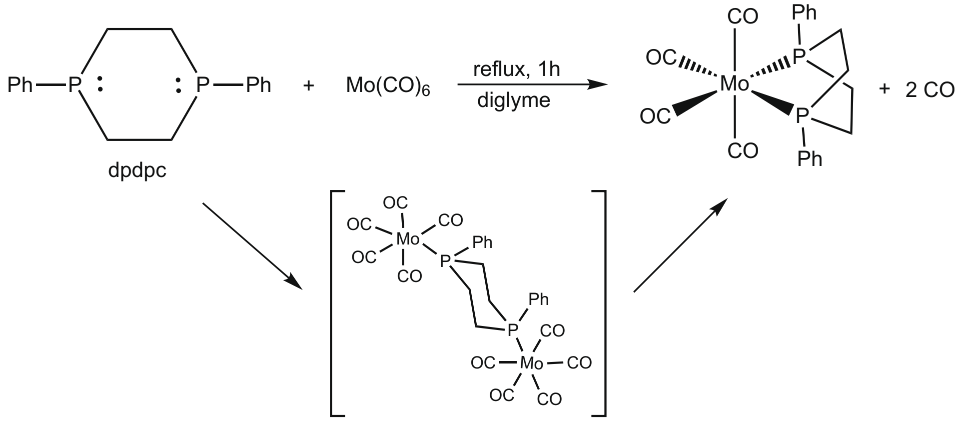

Scheme 1.

to the previously reported Rh dimer/monomer peaks which occurred at 18.0 and 67.0 ppm, respectively [10]. The $^{31}P\{^{1}H\}$ NMR spectra of aliquots of the reaction mixture taken every 5 min show an initial accumulation of the bridged intermediate, which is then converted to the product as the reaction proceeds.

Crystals of the metal complex, suitable for X-ray diffraction studies, were grown by slow evaporation from a saturated CH_2Cl_2 solution of the compound [14]. The structure of the complex shows a distorted octahedral geometry around the metal center from the four carbonyl ligands and two phosphine donors of the dpdpc ligand (Fig. 1). The distortion from octahedral geometry revolves almost solely around the Mo-dpdpc interaction. The P–Mo–P bite angle observed in the structure is 67.130(16)°, the most acute bite angle reported, to date, for this ligand. The *cis* C–Mo–C angles average 90.00(8)° and the *trans* C–Mo–C angle is 179.41(8)°, indicating the carbonyls maintain a nearly perfect octahedral positions around the metal. Clearly the rigid boat confirmation of the dpdpc ligand results in increased structure distortion on the metal center geometry compared to other, more flexible, singly bridged carbon chain ($R_2P–C–C–PR_2$) bidentate ligands. To our knowledge, this complex represents the first reported octahedral complex containing the dpdpc ligand.

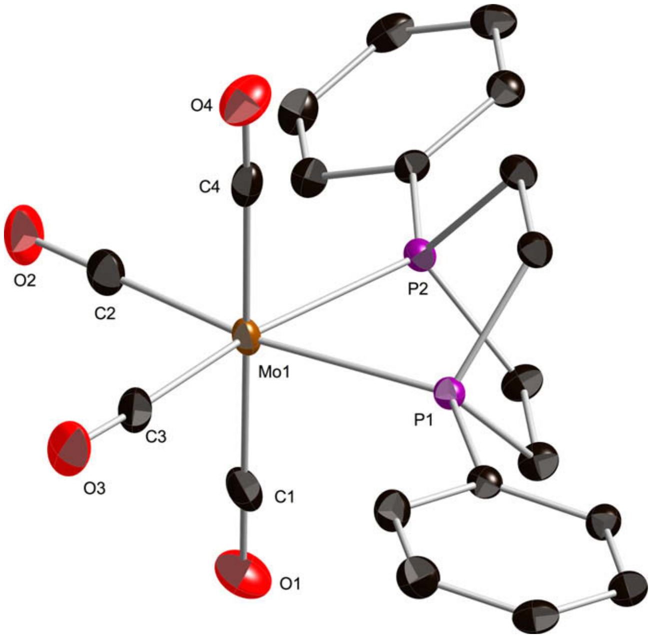

Fig. 1. View of the molecular structure of (dpdpc)Mo$(CO)_4$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Mo(1)–P(1) 2.5020(5); Mo(1)–P(2) 2.5038(5); Mo(1)–C(1) 2.037(3); C(1)–O(1) 1.147(3); Mo(1)–C(4) 2.039(2); C(4)–O(4) 1.148(3); Mo(1)–C(2) 1.991(2); C(2)–O(2) 1.152(3); Mo(1)–C(3) 1.984(2); C(3)–O(3) 1.158(3). Selected bond angles (°): P(1)–Mo(1)–P(2) 67.130(16); C(3)–Mo(1)–C(2) 90.74(8); C(3)–Mo(1)–C(1) 91.94(9); C(2)–Mo(1)–C(1) 89.53(9); P(1)–Mo(1)–P(2) 67.130(16); C(3)–Mo(1)–C(4) 87.51(9); C(2)–Mo(1)–C(4) 90.27(9); C(1)–Mo(1)–C(4) 179.41(8).

The X-ray structure of the complex also indicates the dpdpc ligand does not participate in π-backbonding as strongly as the carbonyl ligands they replaced. The X-ray data show shorter Mo–C bonds, and longer C–O bonds in the carbonyls *trans* from the phosphorus atoms, compared to the carbonyls *trans* from each other (*cis* from the dpdpc ligand). These bond distances indicate an increase in π-backbonding to the carbonyls *trans* to the dpdpc ligand, relative to the carbonyl ligands it replaced.

In summary, a new molybdenum tetracarbonyl complex with the dpdpc ligand was synthesized, representing the first structurally characterized octahedral complex containing the dpdpc ligand. As shown in the crystal structure, the dpdpc ligand is a sterically rigid, bidentate phosphorus ligand that results in an acute P–M–P bond angle upon metal complexation. Similar to previous reports, our studies show the dpdpc ligand is capable of forming both a bridged, dimeric complex with two metal centers or a single monomeric metal complex. We are currently in the process of studying the synthesis and reactivity of similar complexes with a view towards their catalytic activity.

Acknowledgement

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Appendix A. Supplementary material

CCDC 756961 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.01.030.

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[11] Synthesis of Mo(dpdpc)(CO)$_4$: a mixture of Mo(CO)$_6$ (0.262 g, 1.00 mmol), and dpdpc ligand (0.272 g, 1.00 mmol) in 25 mL of diglyme was heated and left to reflux for 1 h. The diglyme was then removed through distillation and the remaining brown oil was dissolved in CH$_2$Cl$_2$, and filtered through celite, leaving a white powder (72 mg, 15% yield). ^{1}H NMR (CDCl$_3$): δ, 7.82–7.49 (multiple peaks, C$_6$H$_5$, 10 H); 2.47, 2.16 (m, –C*H*$_2$–, 8H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ, 27.5 (pseudo t, –*C*H$_2$–, $^2J_{\mathrm{p-c}} = 15.34$ Hz, 4C); 132.5, 132.1, 131.3, 129.1 (multiple peaks, *C*$_6$H$_5$, 12C); 219.5 (m, *C*O – *trans* to dpdpc, 2C); 208.6 (m, *C*O – *cis* to dpdpc, 2C). ^{31}P{^{1}H} NMR (CHCl$_2$): δ, 44.3 (s). IR *C*O-region: 2011.48, 1887.52, and 1841.03 cm^{-1}.

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[14] The intensity data for (dpdpc)Mo(CO)$_4$ were collected at 100 K on a standard SMART 1 K CCD diffractometer using graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. Structures were solved by direct methods using SHELXTL and refined by full-matrix least squares on F^2. Crystal data for Mo(dpdpc)(CO)$_4$: C$_{20}$H$_{18}$MoO$_4$P$_2$; $M = 480.22$, Monoclinic, space group *Pna*2(1), $a = 14.1718(4)$ Å, $b = 8.5612(2)$ Å, $c = 16.7101(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2027.40(10)$ Å^3, $Z = 4$, $D_c = 1.573$ Mg/m^3. $R_1 = 0.0335$, $wR_2 = 0.0590$ (for all data). $R_{\mathrm{int}} = 0.0462$, $R_1 = 0.0259$, $wR_2 = 0.0557$, GOF = 1.015 (49 059 total reflections, 6454 unique reflections where $I > 2\sigma(I)$).