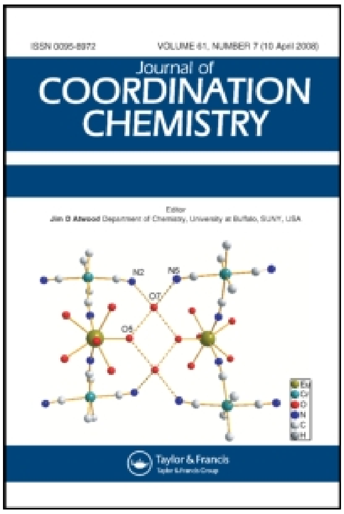

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ZERO VALENT METAL COMPLEXES OF 5,5-DIMETHYL-2-R-1,3,2-DIOXAPHOSPHORINANES†

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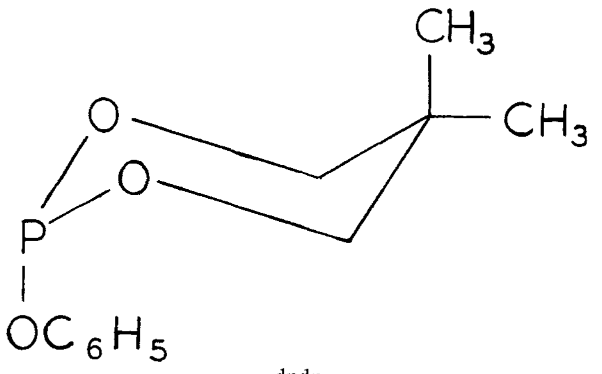
The preparation and characterization of some Ni(0) and Pt(0) complexes of 5,5-dimethyl-2-phenoxy-1,3,2-dioxaphosphorinane is reported. This phosphite, which contains a single six-membered ring, displays donor-acceptor properties intermediate to $P(OCH_2)_3CR$ and trialkyl or triaryl phosphites. The conformation of the ligand in the complexed form is proposed to be a chair ring with an axial phenoxy group.

INTRODUCTION

The characterization and study of metal carbonyl complexes of bicyclic phosphites has led to the conclusion that the behaviour of such ligands as stronger complexing agents than trialkyl or triaryl phosphites is due, in part, to reduced steric demands.[1,2] Studies of analogous complexes of phosphites which possess a single six-membered ring may aid in evaluating this proposal. Phosphites of the general class 2–R–1,3,2-dioxaphosphorinane, which contain such a ring system, have recently been the subject of considerable study directed toward establishment of the configuration and conformation of the free ligand.[3] However, the effect of formation of a coordination complex on ring conformation except with BH_3 ($R = OCH_3$),[4] has not been investigated. Therefore we wish to report the preparation of some zero valent metal complexes of 5,5-dimethyl-2-phenoxy-1,3,2-dioxaphosphorinane(dpdp).



dpdp

EXPERIMENTAL

Materials

Nickel tetracarbonyl was purchased from A. D. Mackay Inc., biscyclopentadienylnickel was purchased from Alpha Inorganics Inc. and was purified according to King,[5] 5,5-dimethyl-2-phenoxy-1,3,2-dioxaphosphorinane (dpdp) was a gift from Hooker Chemical Company. Potassium tetrachloroplatinate(II) was prepared by the method of Keller.[6] 5,5-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinane was prepared by transesterification of 2,2-dimethyl-1,3-propanediol with trimethyl phosphite.[7] All other chemicals were of reagent grade quality.

Instrumentation

The infrared spectra were obtained with a Perkin-Elmer Model 621 double-beam grating spectrophotometer. Spectra were recorded for $\sim 10\%$ chloroform solutions contained in a sodium-chloride cell of 0.17 mm path length and were calibrated with polystyrene film. A Varian Model HA-100 nmr spectrometer was used to obtain the pmr spectra which were recorded at ambient temperature for $\sim 15\%$ chloroform-d or benzene solutions containing tetramethylsilane as an internal standard. Melting points were obtained in open capillary tubes using a Vanderkemp Melting Point Apparatus and are uncorrected. Carbon and hydrogen contents were ascertained by combustion using a F and M Carbon-Hydrogen-Nitrogen Analyzer, Model 185.

Preparations

All preparative steps were carried out under helium and all products were stored *in vacuo.*

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† Abstracted in part from the Ph.D. Dissertation of D. W. Parrott, Ohio University, Athens, Ohio, March 1971.

$Ni(CO)_3(dpdp)$

Nickel tetracarbonyl (1.26 ml, 10 mmole) was added dropwise to a cold (0°), stirred solution of dpdp (1.8 ml, 9 mmole) and pentane (25 ml). After 6 hr, the solvent was removed, the residue dissolved in 10 ml of pentane and the mixture filtered. Cooling the filtrate to −78° yielded 3.15 g (95%) of product. Due to the relative instability and low melting point of the complex, it was stored at −78°. *Anal.* Calcd for $C_{14}H_{15}NiO_6P$: C, 45.57; H, 4.07, Found C, 45.68; H, 4.09.

$Ni(CO)_2(dpdp)_2$

Nickel tetracarbonyl (0.63 ml, 5 mmole) was added dropwise to a cold (0°), stirred solution of dpdp (2.4 ml, 12 mmole) and CCl_4 (25 ml). After 13 hr, the solution was reduced to 1/5 its volume and a few ml of benzene were added. Cooling this solution to 0° gave 2.35 g (83%) of colorless crystals which were recrystallized from 1:1 CCl_4-pentane (mp 88°). *Anal.* Calcd for $C_{24}H_{30}NiO_8P_2$: C, 50.81; H, 5.29. Found: C, 50.24; H, 5.52.

$Ni(CO)(dpdp)_3$

Nickel tetracarbonyl (0.63 ml, 5 mmole) was added dropwise to a stirred solution of dpdp (3.6 ml, 18 mmole) and benzene (20 ml). After 24 hr, the solution was submitted to reflux for 4 hr. Evaporation of the mixture gave 1.95 g (51%) of white crystals which were recrystallized from 1:3 CH_2Cl_2-pentane (mp 145°, dec). *Anal.* Calcd for $C_{34}H_{45}NiO_{10}P_3$: C, 53.35; H, 5.88. Found: C 53.17; H, 5.95.

$Ni(dpdp)_4$

A stirred solution of biscyclopentadienylnickel(0) (0.75 g, 4 mmole), dpdp (5.0 ml, 25 mmole) and benzene (20 ml) was refluxed for 2 hr. The mixture was chromatographed on Fisher 80–200 alumina with benzene as the eluant. The solid obtained by evaporation of the green colored fractions was placed *in vacuo* for 24 hr. The colorless solid thus obtained was dissolved in a few ml of benzene, an excess of methanol was added, and the solution was cooled to 0°. The product (1.6 g, 42%) was isolated by filtration and washed with cold methanol (mp 145°). *Anal.* Calcd for $C_{44}H_{60}NiO_{12}P_4$: C, 54.85; H, 6.12 Found: C, 54.83; H, 6.46.

$Pt(dpdp)_4$

An anhydrous ethanolic hydrazine solution (10% v/v) was added dropwise to a stirred suspension of K_2PtCl_4 (0.83 g, 2 mmole), dpdp (1.6 ml, 8 mmole) and absolute ethanol (20 ml) until the pink color of the suspension disappeared. The mixture was filtered, the filtrate was evaporated and the resulting glass placed *in vacuo* for 24 hr. The glass was dissolved in a few ml of methanol, the solution cooled to 0° and 0.4 g (18%) of white crystalline product was collected by filtration (mp 142–4°). *Anal.* Calcd for $C_{44}H_{60}O_{12}P_4Pt$: C, 48.04; H, 5.46. Found: C, 48.23, H, 5.74.

DISCUSSION

The position(s) of the νCO absorption(s) of the complexes of dpdp (Table I) when compared with those of analogous complexes of other phosphites, indicate that dpdp is intermediate in donor acceptor properties to bicyclic phosphites and trialkyl or triaryl phosphites.[2,8–11] The location of dpdp with respect to other ligands is most evident when the A_1 νCO mode of $Ni(CO)_3(dpdp)$ is compared with the extensive list compiled by Tolman.[11]

TABLE I

Infrared and Pmr Spectral Data

Compound	νCO	Chemical Shifts(δ)					Coupling Constants (Hz)		
		CH_2		CH_3		C_6H_5	J_{gem}	J_{PHax}	J_{PHeq}
		ax	eq	ax	eq				
dpdp	—	4.30	3.40	1.28	0.72	7.10	10.8	3.0	11.0
$Ni(CO)_3(dpdp)$	2086(s) 2014(vs)	4.41	3.67	1.37	0.83	7.17	10	3	17
$Ni(CO)_2(dpdp)_2$	2044(s) 1985(vs)	4.34	3.56	1.33	0.79	7.04	10	> 2	16
$Ni(CO)(dpdp)_4$	1991(vs)	4.19	3.42	1.27	0.69	6.98	10	> 1	15
$Ni(dpdp)_4$	—	3.94	3.16	1.09	0.60	6.98	10	> 1	15
$Pt(dpdp)_4$	—	3.95	3.20	1.07	0.57	7.11	10.5	> 1	15

Although actual data for complexes of the acylic phosphite $P(OC_6H_5)(OCH_3)_2$ is unavailable, the predicted A_1 mode for the monosubstituted nickel carbonyl complex of this ligand is 2081 cm^{-1}.[11] Thus it appears that introduction of a $(OCH_2)_2C(CH_3)_2$ group, which forms a six-membered ring, in place of two acyclic OCH_3 groups provides inhanced ligand properties. It is interesting that the phosphite $C_6H_5OP(OCH_2)_2$ which contains a five-membered ring occupies a nearly identical position as dpdp in the ligand series.[11] The most likely conformation for dpdp (*vide infra*), a chair ring with an axial OC_6H_5, yields the smallest cone angle for the ligand donor site. Although introduction of a ring has slightly reduced potential steric interaction between a metal and the phosphorus of dpdp relative to $P(OC_6H_5)(OCH_3)_2$, the increased ligand properties of dpdp are also attributable to an electronic effect which has its origin in the decrease in average POC angle that occurs as a result of constraint.[3,12] The complimentarity of these two effects makes identification of the component of major importance difficult. The ability of monocyclic phosphites to stabilize the zero oxidation state of metals is evidenced by the facile preparation of $Ni(dpdp)_4$ and $Pt(dpdp)_4$.

Preparation of complexes of 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (dmdp) would provide a second monocyclic system for evaluation. Data for a considerable number of analogous complexes of $P(OCH_3)_3$ and $P(OCH_2)_2CR$ is available for comparison.[2,8-10] The reaction of nickel carbonyl with dmdp gave di- and trisubstituted complexes as identified by their infrared spectra (νCO, ~2035(s); ~1972(vs) and 1969(vs), respectively). All attempts to isolate these complexes yielded materials for which acceptable analytical results could not be obtained. From the crude infrared data it is evident that substitution of OCH_3 for the OC_6H_5 group of dpdp yields a poorer ligand as is expected from electronic considerations which are illustrated by a comparison of the properties of $P(OCH_3)_3$ with $P(OC_6H_5)_3$.[8,9,11] The position of dmdp between $P(OCH_3)_3$ and $P(OCH_2)_3CR$ in donor properties is proposed to result from decreased steric and increased electronic effects similar to that noted for dpdp.

Assignments for the pmr spectrum of the ligand (Table I) for which the equatorial methylene group appears as a triplet of triplets, the axial methylene group as a doublet of doublets and the single axial methyl resonance is broader and at lower field than the equatorial methyl resonance are in agreement with those previously made.[13,14] For the complexes, assignment of the proton resonances is facilitated by the different coupling constants associated with the methylene multiplets and the variation in line width of the two methyl resonances. Formation of a monosubstituted complex produces a downfield shift for all protons, the magnitude of which is similar for both methyl groups but considerably greater for the axial than equatorial methylene protons. Relative to $Ni(CO)_3(dpdp)$, additional CO replacement is accompanied by increased shielding of all ligand resonances. A similar behaviour is observed when the ligand system $P(OCH_2)_3CR$ is employed[2] and this suggests that the phosphorus becomes a poorer *sigma* donor and/or a better *pi* acceptor as more phosphites are added to the metal.

Complexation of dpdp causes an increase in $J_{PH_{eq}}$ and the disappearance of $J_{H_{eq}H_{eq}}$ which may indicate a slight change in ring conformation. Increased substitution produces a narrowing of the axial methylene resonance as a result of a decrease in $J_{PH_{ax}}$. For the tri- and tetrasubstituted complexes, a loss of fine structure for the equatorial methylene resonance results from phosphorous-phosphorus coupling ($Ni(dpdp)_4 > Ni(CO)(dpdp)_3$) and prevents the determination of $J_{PH_{eq}}$ with an accuracy $> \pm 2$ Hz.

The conformation of dpdp in the complexed form is proposed to be the same as X-ray methods have determined for its oxide; chair ring with axial phenoxy group.[15] The arguments concerning HCCCH and POCH coupling constants used by White *et. al.*[3] and Bentude and Hargis[16] for 5,5-dimethyl-1-R-1,3,2-dioxaphosphorinanes may be applied in a similar manner to the complexes reported herein to exclude boat and twist conformers from consideration. Since dpdp is reported to exist as a single conformer from —40 to 155°[13] and complex formation with $Ni(CO)_4$ at 0–20° would be expected to occur without inversion, the phenoxy group is expected to occupy the axial position in the complexed as well as the free form.

Studies of the effect of solvent on the chemical shift positions of some 2-oxo-2-R-1,3,2-dioxaphosphorinanes indicated that methyl groups at the 5 position are preferentially more shielded when located *trans* to the R group (*cis* to the phosphoryl group) when the solvent is changed from $CDCl_3$ to C_6H_5.[17,18] Since line widths unequivocally identify which resonance belongs to the axial and equatorial methyl groups, then solvent effect studies can provide a test of our contention that the phenoxy moiety is axial to the ring. If the phenoxy group is axial, the equatorial methyl position (the methyl *trans* to the phenoxy) should be preferentially shielded with respect to the axial methyl group. If a reverse preferential shielding should occur, then the phenoxy is located equatorial to the ring. The $\Delta\delta$ values ($\Delta\delta = \delta_{CDCl_3} - \delta_{C_6H_6}$) for the equatorial and axial methyl groups of $Ni(CO)_3$(dpdp) are 58 and 27 Hz, respectively, which substantiates our assignment of the phenoxy group to the axial position. Similar $\Delta\delta$ values are reported for the oxide of dpdp[17] wherein the phenoxy group has been established by X-ray crystallography to be axial.[15]

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