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Bicyclic Aminophosphites as N-Donors towards W(VI) Oxoalkoxides

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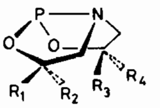
The constrained structure of bicyclic aminophosphites L *3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3,3,0)octane* (L_a) *and 3,7-dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3,3,0)octane* (L_b) *leads to the restoration of the donor properties of the nitrogen adjacent to the phosphorus atom. This is illustrated by the facile formation of 1:1 adducts with tungsten(VI) alkoxide* $WO(OMe)_4$*, the metal attaining hexacoordination by attachment of the ligand through the nitrogen. Oxido-reduction reactions in the coordination sphere between the W(VI) and P(III) centers, which provide bicyclic alkoxyphosphorane, prevented the isolation of these* $WO(OMe)_4 \cdot L$ *adducts. Stabilization was achieved by additional coordination of the phosphorus lone pair by a* BH_3 *moiety. A mixed adduct* $WO(OMe)_4 \cdot L_a \cdot BH_3$*, which also represents the first tungsten oxoalkoxide adduct reported so far, was isolated. The bicyclic aminophosphites* L *behave as P-donors towards less hard Lewis acids, even W(VI) derivatives. Thus* $WOCl_4(L_a)_2$, cis-$PtCl_2(L_a)_2$ *and* $[Rh(\mu\text{-}Cl)(C_2H_4)L_a]_2$ *were isolated and characterized. The large metal phosphorus coupling constants compare favorably with those of common phosphites.*

Introduction

Phosphorus compounds having P–N bonds, in spite of the presence of two potential donor sites, usually act only as P-donors [1]. In general, nitrogens adjacent to phosphorus are sp^2 hybridized and the lone pair in the p-orbital is not basic [2]. Constrained structures, however, in which the nitrogen center is prevented from having a planar configuration, lead to restoration of its donor properties [3].

Compounds such as bicyclic aminophosphites *L* illustrate one way of forcing the nitrogen atom to keep a pyramidal configuration.



$R_1 = R_2 = R_3 = R_4 = Me$ (L_a)

$R_1 = R_3 = H$; $R_2 = R_4 = Me$ (L_b)

As expected, the nitrogen atom recovers its donor ability, providing stable $N-BH_3$ as well as $N-BF_3$ adducts [4]. Bicyclic aminophosphites L_a and L_b behave as bidentates towards the BH_3 moiety; on the contrary, only 1:1 adducts form with the harder BF_3 acid, even when used in excess. However, despite the availability of the nitrogen lone pair for coordination with boron derivatives, no evidence for interaction through the nitrogen atom has been found so far with transition metal derivatives. The ligands used, 3,7-dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3,3,0)octane (L_b) and 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane (L_a), act only as monodentate P-donors towards Mo(0), W(0) and Mo(II) carbonyl [5a] or Fe(II) [5b] derivatives. Examples of coordination to a metal of a tricoordinate nitrogen directly linked to a phosphorus(III) atom remain scarce: the only well- (X-ray)-established case is that of a W(0) tetracarbonyl phosphonitrilic adduct [6]. Coordination through the phosphorus atom in addition to the nitrogen atom has also been suggested to account for the stoichiometry of Ni(II) and Zn(II) bis and tris(aziridino)phosphane adducts [7], or for the stability of the 1,2-dimethyl-1,2,3-diazaphosphenium tetracarbonyliron(0) cation [8]. Thus, the coordination of a nitrogen in α to a phosphorus(III) center seems to be favored by chelation, as also observed and well established for the transition metal–phosphoranide derivatives [9].

We wish now to report the formation of bicyclic aminophosphites L_a and L_b N-adducts with $WO(OMe)_4$. Their isolation was achieved as mixed $WO(OMe)_4 \cdot L \cdot BH_3$ complexes after coordination of the P lone pair through a BH_3 moiety, thus preventing oxidoreduction reactions between the P(III)–W(VI) centers. Classical P-adducts $WOCl_4(L_a)_2$, *cis*-$PtCl_2(L_a)_2$ and $[Rh(\mu\text{-}Cl)(C_2H_4)L_a]_2$ were obtained when the bicyclic aminophosphites were allowed to react with less hard metallic species.

Results and Discussion

In order to evaluate the donor ability of the nitrogen of the bicyclic aminophosphite ligands towards

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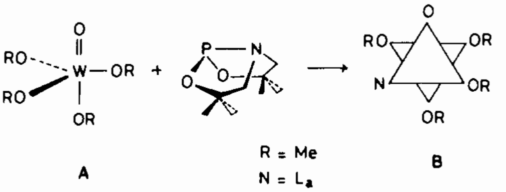
transition metal derivatives, we turned to species with relatively high oxidation states and/or NMR active nuclei, and especially with spin I = ½. Indeed, although ^{31}P coordination chemical shifts ($\Delta = \delta^{31}$P complex − δ^{31}P free ligand) are generally found to be positive for P-donors [10], they do not provide unambiguous information regarding the bonding modes for ambidentate ligands. A better indication of the coordination site in the absence of X-ray data appears to be whether or not metal–phosphorus $^1J_{M-P}$ constants exist. On the other hand, the coordination properties of these constrained aminophosphites were examined using mainly L_a, although its steric hindrance is higher than that of L_b [5]. Indeed, L_b exists as two diastereoisomers (α and β), which may complicate the NMR interpretation.

Tungsten is a 'magnetically useful' metal (^{183}W: I = ½, 14.3%). The variety of oxidation states and derivatives available covers a large scale of acceptor properties, and makes them attractive for our purpose. The reaction between WCl_4 and L_a in CH_2Cl_2 led to the isolation of $WOCl_4(L_a)_2$. However, the ^{31}P data ($\delta^{31}P = 168$ ppm, $^1J_{^{183}W-^{31}P} = 488$ Hz) established that the two ligands occupy magnetically equivalent positions, and interact with the metal through the phosphorus. The large phosphorus–tungsten coupling constant is in agreement with the data obtained for tungsten–phosphite adducts [11].

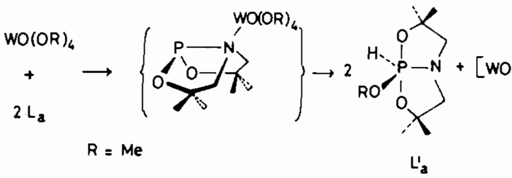
Alkoxides are known to behave as harder metallic centers than the corresponding halides [12]. Reaction between $WO(OMe)_4$ and L_a in toluene showed the formation of a new species at 140 ppm in the ^{31}P NMR. The peak of the free ligand (162 ppm) appears only if the ligand to metal molar ratio is higher than 1. No metal–phosphorus coupling constant could be detected, even at low temperature (−60 °C). Although the peak at 140 ppm may be attributed to the dimer of the original ligand [13], ^{1}H monitoring data excludes this hypothesis but supports the formation of a 1:1 adduct involving nitrogen coordination. In non-polar solvents, the monomeric $WO(OMe)_4$ adopts a bipyramidal configuration (structure A), already rigid at room temperature, as illustrated by the observation in the ^{1}H NMR of inequivalent alkoxo groups (δ = 4.62 and 4.55 ppm in toluene, 3:1). No other isomers were detected at lower temperatures. Addition of the bicyclic aminophosphites is immediately followed by the formation of a new tungsten–alkoxo species characterized by resonances at 4.60, 4.57 and 4.53 ppm, whose relative area 2:1:1 remains constant with dilution. The NMR pattern of the ligand shows that the bicyclic structure is maintained. These data are in agreement with the formation of $WO(OMe)_4 \cdot L_a$ of structure B, the ligand being attached to the metal by the nitrogen pair only (eqn. 1):



(1)

$WO(OMe)_4 \cdot L_a$ is the first complex reported so far, to our knowledge, for W(VI) oxoalkoxides. Its formation is consistent with that of $MoO(O^iPr)_4 \cdot py$, recently described [14].

However, despite the facile formation of the $WO(OMe)_4 \cdot L_a$ adduct, attempts on isolation failed as a result of instability towards oxidoreduction reactions, induced by catalytic amounts of protons in the medium. The ^{1}H as well as the ^{31}P NMR indicated the conversion of the bicyclic aminophosphite to bicyclic alkoxyphosphorane L'_a ($\delta^{31}P = -37$ ppm, $^1J_{P-H} = 807$ Hz) by an oxidative addition of methanol to the phosphite according to eqn. 2:



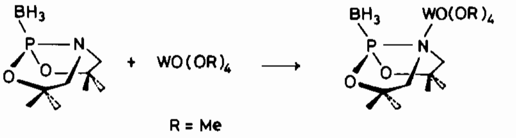
(2)

The P(III)–P(V) transformation was favoured by the use of protic solvents such as CH_2Cl_2 or MeCN, as well as higher temperatures (up to 60 °C). Similar behaviour was observed for L_b, whose N-coordination with $WO(OMe)_4$ (δ = 132(α), 130(β); 4:1) was also followed by the appearing of the phosphorane (δ = −39 ppm; $^1J_{P-H} = 812$ Hz). Although bicyclic alkoxyphosphoranes have already been detected in solution by ^{31}P NMR [15], they were not isolated. We were able to obtain L'_a in its free state as well as attached to a metal, in the P(III) tautomeric form; details will be published elsewhere.

In order to obtain more stable bicyclic aminophosphite adducts, we turned to tungsten–alkoxides in which the alkoxo groups should be less labile, or to less reductible alkoxides. The chlorooxoalkoxide $WO(OMe)_3Cl$ was indeed also found to coordinate L_a, through the nitrogen center ($\delta^{31}P = 142$ ppm), but the lability of the tungsten alkoxo species remains too high to prevent the formation of the phosphorane and allow the isolation of a pure aminophosphite adduct.

Finally, stabilisation of the tungsten N-adducts was best achieved when the phosphorus pair was already engaged in a coordination bond, with a borane moiety for instance. Attempts to coordinate the phosphorus lone pair of the $WO(OMe)_4 \cdot L_a$ complexes through addition of $BH_3 \cdot THF$ led mainly to reduction of the metal. However, the addition of 1 equivalent of $WO(OMe)_4$ to a solution of $L_a \cdot BH_3$

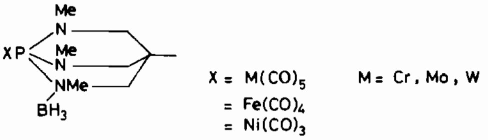
in toluene shows further coordination of the phosphorus ligand without decomplexation of the BH_3 moiety. The ^{31}P data indicate that the quadruplet of the original $L_a \cdot BH_3$ (δ = 154 ppm, $^1J_{P-B}$ = 88 Hz) is shifted to higher field (δ = 126 ppm; J_{P-B} = 89 Hz); no bis(borane) adduct was detected. The phosphorus–boron coupling constant established that the BH_3 group remains on the phosphorus center; moreover, no loss of B_2H_6 occurs during the reaction. ^1H data, especially the pattern in the alkoxo region (δ = 4.80, 4.81, 4.84 (2:1:1) confirm that the high field shift observed by ^{31}P can be attributed only to coordination of $WO(OMe)_4$ to the nitrogen pair, according to eqn. 3:



(3)

The mixed $WO(OMe)_4 \cdot L_a \cdot BH_3$ adduct is now stable*, and its isolation can be achieved. Microanalysis as well as the spectroscopic data are consistent with the above formula. That the isolated solid does not consist of mixed crystals of $WO(OMe)_4$ and the monoborane adduct is indicated by the mass spectrum, which exhibits the expected molecular ion (M/e = 526).

Bidentate behaviour of constrained aminophosphanes towards both borane and a transition metal center has also been reported, but the soft metallic center is attached to the phosphorus [16] while the BH_3 moiety is linked to a nitrogen:



(4)

Niobium and tantalum alkoxides are much more stable towards reduction than the tungsten alkoxides, and no reduction by ligands has been reported so far, even under drastic conditions. Moreover, among the large number (more than 30) of potential mono or bidentate ligands tested towards $[M(OCH_3)_5]_2$ (M = Nb, Ta), only a few amines (NH_3, C_5H_5N, ...) or oxo-type donors (OER_3 E = N, P, As) were able to compete with the bridge formation of the dimers, giving 1:1 adducts [12]. Unfortunately, no formation of any adduct could be detected between various bicyclic aminophosphites, and the tantalum alkoxides – $[Ta(OMe)_5]_2$ or the partially depolymerised $Ta(O^iPr)_5$ [17]; these are harder than the corresponding niobium derivatives, and were therefore expected to favour the complexation of ligand L_a or L_b.

Reactions between bicyclic aminophosphites and other magnetically active metal derivatives, as for instance Pt(II) or Rh(I), only offered adducts in which the ligand is attached through the phosphorus. Indeed, reactions between L_a and *cis*-$PtCl_2(PhCN)_2$ in methylene chloride, provided *cis*-$PtCl_2(L_a)_2$. Despite a high-field ^{31}P shift (δ = 110 ppm), P-coordination is involved, as indicated by the coupling constants ($^1J_{^{195}Pt-^{31}P}$ = 5800 Hz, $^2J_{P-P}$ = 30 Hz). The metal–phosphorus coupling constant compares with those found for platinum(II) phosphite adducts [18]. Similarly, the reaction between $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$ and L_a in toluene gives only P-adducts, even if the reaction occurs with only one ligand per metal. In this case, $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_2(L_a)_2$ displaying equivalent phosphorus ligand (^{31}P: 171 ppm, $J_{^{103}Rh-^{31}P}$ = 200 Hz) was isolated.

Experimental

The various reactions were performed under dry argon using Schlenk tube techniques. The solvents were purified by standard methods. The bicyclic aminophosphites [5, 13] and their borane adducts [4], $WOCl_4$ [19], $WO(OMe)_4$ [20], $Ta(OR)_5$ [17], *cis*-$PtCl_2(PhCN)_2$ [21], $[RhCl(C_2H_4)_2]_2$ [22], were obtained according to the literature. ^1H as well as ^{31}P NMR spectra were registered on a WH-90 BRUKER spectrometer operating in the Fourier transform mode.

^{31}P chemical shifts were given towards H_3PO_4 (85%) as external reference. The IR spectra were measured as nujol mulls on a 577 Perkin-Elmer spectrometer. Mass spectra were performed on a R10 RIBERMAG 10 spectrometer. The microanalyses were effected by the Centre de Microanalyses du CNRS.

Synthesis of $WOCl_4 \cdot (L_a)_2$

A solution of 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane (665 mg, 3.63 mmol) in 6 ml CH_2Cl_2 was added to a suspension of $WOCl_4$ (620 mg, 1.82 mmol) in 15 ml CH_2Cl_2 at room temperature. The colour of the reaction mixture immediately turned from red to blue-green. After stirring for about 90 min. and filtration, the solution was concentrated to about 7 ml. Addition of toluene precipitated $WOCl_4 \cdot (L_a)_2$ (910 mg, 94%) as a blue-green powder. *Anal.*: Found C, 27.05; H, 4.53; N, 3.78; Cl, 18.55. Calcd.: $C_{16}H_{32}N_2O_5P_2Cl_4W$: C, 26.67; H, 4.48; N, 3.89; Cl, 19.72. IR: 920s ($\nu_{W=O}$);

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*Although stabilization towards oxido-reduction involving the P(III) center was achieved by this procedure, the $WO(OMe)_4$ adduct remains of low stability despite the low steric hindrance of ligands of type *L* [5]. Evolution to dioxo-alkoxides by elimination of dialkylether – favoured by solvents such as CH_2Cl_2 – was possible.

340 sh, 320 vs, 300 vs, 290 sh, 250 m (ν_{W-Cl}). ^{31}P NMR (CH_2Cl_2): 168 ppm ($^1J_{W-P}$ = 488 Hz).

Synthesis of $WO(OMe)_4 \cdot L_a \cdot BH_3$

A solution of the monoborane adduct $L_a \cdot BH_3$ (110 mg, 0.55 mmol) in 2 ml MeCN was added to a solution of $WO(OMe)_4$ (180 mg, 0.55 mmol) in MeCN. After about 30 min the green-yellow solution was evaporated to dryness, leaving a microcrystalline powder.

Anal.: Found: C, 27.12; H, 5.45; N, 2.56; B, 2.02. Calcd: $C_{12}H_{29}O_7NPBW$: C, 27.37; H, 5.56; N, 2.66; B, 2.10. IR: 2400 br (ν_{B-H}), 915 s ($\nu_{W=O}$), 545 (ν_{W-O}). ^{31}P NMR (To) 126 ppm ($^1J_{P-B}$ = 89 Hz). Mass spectrometry: M = $WO(OMe)_4 \cdot L \cdot BH_3$ M (8%), M$-BH_3$ + H_2 (8%), M$-BH_3-OMe_2$ (16%), M$-BH_3-2C_2H_6$ (16%), $WO_7PC_6H_2$ (100%), $WO_2(OMe)_2$ + H_2 (40%) ($L \cdot BH_3$ + H_2) (5%) L$-C_3H_5$ (18%).

Synthesis of cis-$PtCl_2(L_a)_2$

A solution of *cis*-$PtCl_2(PhCN)_2$ (462 mg, 0.98 mmol) in 12 ml CH_2Cl_2 was added at room temperature to a solution of 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3,3,0)octane (3.70 mg, 1.96 mmol) in 5 ml toluene. A white precipitate (which re-dissolved progressively) appeared immediately upon addition, and finally a colourless solution was obtained. After 60 min the solution was concentrated to about 3 ml, and toluene (7 ml) was added. Precipitation started immediately. *Cis*-$PtCl_2(L_a)_2$ (416 mg, 66%) was obtained as a white microcrystalline powder after filtration and washing with toluene. *Anal.*: Found: C, 29.25; H, 5.07; N, 4.18; P, 9.52. Calcd: $C_{16}H_{32}N_2O_4P_2Cl_2Pt$: C, 29.81; H, 5.01; N, 4.35; P, 9.63. IR: 300 vs, 290 m (ν_{Pt-Cl}). ^{31}P NMR (CH_2Cl_2): 110 ppm ($^1J_{Pt-P}$ = 5800 Hz; $^2J_{P-P}$ = 30 Hz).

Synthesis of $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_2(L_a)_2]$

A solution of 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3,3,0)octane (165 mg, 0.87 mmol) in 2 ml toluene was slowly added to a solution of $[RhCl(C_2H_4)_2]_2$ (170 mg, 0.87 mmol) in the dark at room temperature. After 45 min the gaseous evolution was stabilized, and lemon-coloured crystals were removed by filtration. A second crop of crystals was obtained by adding hexane (≅3 ml) and storing in the cold. Finally 230 mg (75%) of $Rh_2(\mu\text{-}Cl)_2(C_2H_4)_2(L_a)_2$ was isolated as light, air-sensitive yellow crystals. *Anal.*: Found: C, 33.20; H, 5.58; N, 4.02. Calcd: $C_{10}H_{20}NO_2PClRh$: C, 33.75; H, 5.67; N, 3.94. IR: 1620 ($\nu_{C=C}$); 300 m (ν_{Rh-Cl}). ^{31}P NMR (CH_2Cl_2): 171 ppm ($^1J_{Rh-P}$ = 199 Hz). ^{1}H NMR ($CDCl_3$): 5.25 br (C_2H_4), 3.57–3.17 m (CH_2); 1.46, 1.40 (CH_3). Mass spectrometry (chemical ionization): $[Rh(\mu\text{-}Cl)(C_2H_4)L]_2-L-C_2H_6$ (2%), LRh_2-NH_3 or LRh_2O (85%). LRH_2 (35%); $LRhPO_2$ (7%), $RhP_2O_3NC_8H_{12}$ (7%), Rh_2OH or RH_2NH_4 (100%), Rh_2 (97%), LH (16%).

All new complexes isolated were found to be soluble in MeCN or CH_2Cl_2.

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