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THE USE OF CHLOROALKYLDICHLOROARSINES IN HYBRID LIGAND SYNTHESIS. THE PREPARATION OF BUT-3-ENYLBIS(3-DIMETHYLARSINOPROPYL)ARSINE AND 3-DIMETHYLARSINOPROPYLBIS(BUT-3-ENYL)ARSINE, AND THEIR REACTION WITH NICKEL(II) SALTS TO FORM PENTACOORDINATE COMPLEXES. NOVEL NICKEL(II)–OLEFIN BONDS

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Summary

Routes have been developed to the hitherto unobtainable arsine-olefin ligands $(CH_2{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ ($n = 1$, tasol, but-3-enylbis(3-dimethylarsinopropyl)arsine; $n = 2$, dasdol, 3-dimethylarsinopropylbis(but-3-enyl)arsine) by making use of the difference in reactivity between the Cl–C and As–Cl bonds in the precursor $Cl(CH_2)_mAsCl_2$ ($m = 2,3$) molecules. Thus, the triarsine obtained by reaction of 2-chloroethyldichloroarsine with the Grignard reagent of 3-chloropropyldimethylarsine yields 2-chloroethylbis(3-dimethylarsinopropyl)arsine, from which tasol is obtainable by subsequent reaction with either the Grignard reagent of vinyl bromide or, preferably, with vinyllithium. Similarly, 3-chloropropyldichloroarsine reacts with the Grignard reagent of 4-chlorobut-1-ene to form 3-chloropropylbis(but-3-enyl)arsine which, on reaction with sodium dimethylarsenide yields dasdol. The tasol ligand reacts with nickel(II) salts to form $[NiX(tasol)]^+$ (X = Cl, Br) and $[NiI_2(tasol)]$, the former are trigonal bipyramidal and contain a nickel(II)–olefin bond, and the latter are square pyramidal containing a $[NiI_2As_3]$ coordination sphere. In addition, tasol forms a number of polynuclear complexes with nickel(II). The dasdol ligand acts as a bidentate arsine to form only $[NiX(dasdol)_2]^+$. The formation of novel nickel(II)–olefin bonds in the $[NiX(tasol)]^+$ cations is discussed.

There has been a good deal of interest in chelating ligands containing tertiary phosphines or arsines and an olefinic group. These have been of three types, viz.: potentially bidentate (I) [1–10], potentially tridentate (II) [6,11,12], or potentially quadridentate (III) [3,13–15].

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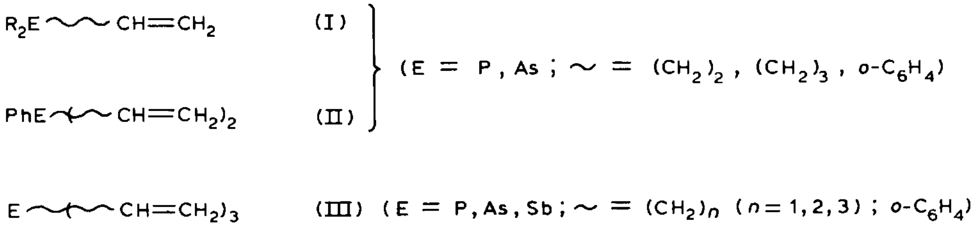


$R_2E\sim\sim CH{=}CH_2$ (I)

$PhE(\sim\sim CH{=}CH_2)_2$ (II)

(E = P, As ; ~ = $(CH_2)_2$, $(CH_2)_3$, o-C_6H_4)

$E(\sim\sim CH{=}CH_2)_3$ (III) (E = P, As, Sb ; ~ = $(CH_2)_n$ (n = 1,2,3) ; o-C_6H_4)

There remains one, virtually unexplored, area: that of a systematic study of a series of quadridentate ligands of formula IV:

$(CH_2{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$($n = 3$, astol;
(IV) $n = 2$, dasdol;
$n = 1$, tasol)

Of the preparative routes [16] ligands containing P or As donors in addition to an olefin donor Grignard reagents are important:

$(ol)_{3-n}ECl_n + nXMgR \rightarrow (ol)_{3-n}ER_n$

In principle this is open to numerous permutations, especially with respect to the nature of R, but this has been restricted, in practice, to the case where R is phenyl or alkyl. However, ligands of great potential would arise if the substituent R group contained a soft donor atom, i.e., a ligand of type IV. Of the ligands so far reported most contain only one soft Group VB donor, and these are unlikely to be good chelating ligands towards any but the strongest soft acids.

The importance of metal–olefin coordination in a large number of industrial processes is well documented [17]. However, the metals used in such processes are expensive, and in order to soundly base a system of catalysis on less expensive metals, e.g. nickel(II), corresponding to d^8 systems such as Rh^I, Pd^{II}, Pt^{II}, it is important to delineate the conditions under which, for example, a nickel(II)–olefin bond may be formed. We have thus developed a series of arsine-olefin ligands of type IV which do exhibit a rich coordination chemistry [14,18]. Because the organic chemistry involved is quite intricate, we report here the synthetic methods adopted to produce the ligands, and we find that, under certain conditions, nickel(II)–olefin bonds may be formed, and it thus does appear that "hard" acids such as Ni^{II}, when suitably modified by such donors as trialkylarsines, may be persuaded to coordinate olefins. A preliminary account of this work has appeared [18].

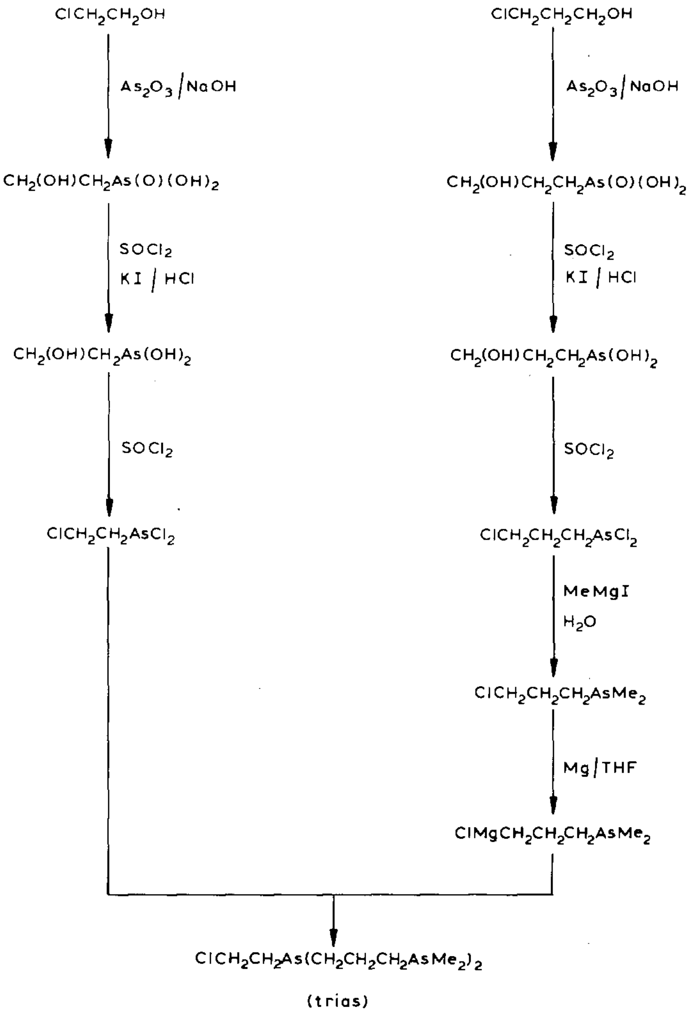
Results and discussion

The ligands

Of the three ligands listed, IV, the synthesis of astol, $As(CH_2CH_2CH{=}CH_2)_3$, has already been reported in detail [14]. This proved to be quite straightforward, but the syntheses of dasdol, $(CH_2{=}CHCH_2CH_2)_2AsCH_2CH_2CH_2AsMe_2$, and tasol $CH_2{=}CHCH_2CH_2As(CH_2CH_2CH_2AsMe_2)$, presented some interesting problems.

We found that a key intermediate is 2-chloroethylbis(3-dimethylarsinopropyl)-arsine, trias, the preparation for which is outlined in Scheme 1.

In the synthesis of ligands of type R'_nAsR_{3-n} it is not usually possible to obtain



SCHEME 1

selective stepwise substitution of $AsCl_3$ by Grignard synthesis. The As–Cl bond is very reactive towards Grignard reagents, and even in dilute solution and at low temperatures reaction of trichloroarsine with RMgCl species usually gives a mixture of all three substitution products, i.e. $RAsCl_2$, R_2AsCl and R_3As.

An alternative route uses the difference in reactivity between the As–Cl and the C–Cl bonds [19,20] and this was the route adopted.

The reaction of 3-chloropropanol and sodium arsenate gave 3-hydroxypropylarsonic acid as a pale yellow oil. Excess thionyl chloride was used to convert 3-hydroxypropylarsenous acid to 3-chloropropyldichloroarsine.

The synthesis of 2-chloroethyldichloroarsine was carried out using an identical route. It is interesting to note that the yields of 2-chloroethyldichloroarsine were much inferior to those of 3-chloropropyldichloroarsine. The difficulty in the preparation and manipulation of arsines with substituted backbones has been observed before [16]. The reaction

$$XCH_2CH_2AsR_2 \rightarrow C_2H_4 + XAsR_2$$

is a major competing side reaction, and considerable quantities of $AsCl_3$ were collected during the distillation.

Trias

The novel triarsine $ClCH_2CH_2As(CH_2CH_2CH_2AsMe_2)_2$ (trias) was prepared by the controlled addition of a Grignard reagent of 3-chloropropyldimethylarsine to 2-chloroethyldichloroarsine in ether. To ensure the most efficient substitution of both As–Cl bonds, and to minimise the production of a fully substituted tetraarsine, the molar quantities of 2-chlorodichloroarsine were kept in slight excess (calculated on the basis of a 65% efficiency of Grignard synthesis).

The alkyl triarsine is an excellent chelating agent for d^7 and d^8 metal ions and bears an obvious relationship with tas, $MeAs(CH_2CH_2AsMe_2)_2$ [21], and with tasp, $PhAs(CH_2CH_2CH_2AsMe_2)_2$ [22]. Furthermore, its coordination chemistry provides an excellent comparison for the coordination chemistry of tasol.

Tasol

It is possible to convert trias to tasol by two methods, viz.:

$$ClCH_2CH_2As(CH_2CH_2CH_2AsMe_2)_2 + MCH{=}CH_2 \xrightarrow{THF}$$

$$(M = Li \text{ or } Br\text{-}Mg) \qquad CH_2{=}CHCH_2CH_2As(CH_2CH_2CH_2AsMe_2)_2$$

On the one hand, a Grignard reagent of vinyl bromide may be used but better yields of tasol were obtained by using vinyllithium; although the solid is pyrophoric, a hexane solution can be safely handled in a syringe. The reaction with trias is smooth and convenient and the reaction products are easy to separate.

Tasol was obtained as a pale yellow air-sensitive oil. Although volatile impurities are readily removed under vacuum, it proved impossible to distil the product; tasol begins to decompose quite rapidly at 180°C before boiling. The ^1H NMR (Table 1) spectra of neat tasol are consistent with the formulation, consisting of a peak at 1.53 ppm which is assigned to the $AsMe_2$ methyl hydrogens, and a complex doublet structure at 2.2 ppm which is assigned to the CH_2 groups of the backbone linkages. Both absorptions are present in the spectrum of 3-chloropropyldimethylarsine (Table 1), along with a complex triplet structure ca. 3.8 ppm which is assigned to the

TABLE 1

^1H NMR SPECTRUM OF TASOL AND SOME PRECURSORS δ(ppm)

	$AsMe_2$	CH_2	olefinic H	$ClCH_2$
$ClCH_2CH_2CH_2AsMe_2$	1.53	2.2 [a]		3.85 [b]
$ClCH_2CH_2CH{=}CH_2$		2.1 [c]	4.7 [c] 5.5 [c]	
tasol	1.59	2.4 [a]	4.4 [a] 4.9 [c]	3.2 [d]
dasdol	1.45	1.97 2.4 [c]	4.5 [b] 5.0 [c]	3.2 [e]

[a] Doublet structure. [b] Triplet structure. [c] Complex multiplet. [d] Complex multiplet, CH_2 of the butenyl group. [e] Quartet structure.

$ClCH_2$-methylene protons. A similar very weak triplet structure is present in the spectrum of tasol ca. 3.6 ppm; integration indicates that this trias impurity is present to the extent of ca. 2%. Two relatively weak absorptions in the tasol spectrum are assigned to the olefinic protons; a doublet structure at 4.4 ppm and a complex multiplet at about 4.9 ppm.

Dasdol

The route employed in the synthesis of 3-dimethylarsinopropylbis(but-3-enyl)arsine, dasdol, is outlined:

$$Mg + CH_2{=}CHCH_2CH_2Cl \xrightarrow[N_2]{THF} CH_2{=}CHCH_2CH_2MgCl \xrightarrow{ClCH_2CH_2CH_2AsCl_2}$$

$$ClCH_2CH_2CH_2As(CH_2CH_2CH{=}CH_2)_2 \xrightarrow[liq.\ NH_3]{NaAsMe_2\ [23]}$$

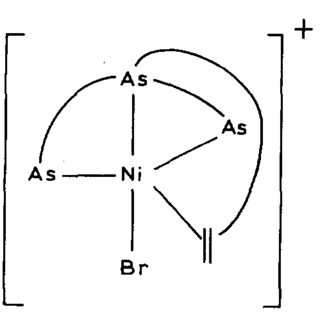
$$Me_2AsCH_2CH_2CH_2As(CH_2CH_2CH{=}CH_2)_2$$

This synthesis provides a further illustration of the adaptability of the $Cl(CH_2)_nAsCl_2$ intermediates in hybrid ligand synthesis. The pure dasdol product was obtained as a colourless air-sensitive oil, b.p. 128°C/0.1 mmHg. The ^1H NMR spectrum of the pure liquid, Table 1, consists of four main areas of absorption, and bears a considerable resemblance to that of tasol and has been assigned accordingly. The spectrum indicates the presence of a trace of the precursor, $ClCH_2CH_2CH_2As(CH_2CH_2CH{=}CH_2)_2$, (a poorly resolved complex multiplet around 3.8 ppm).

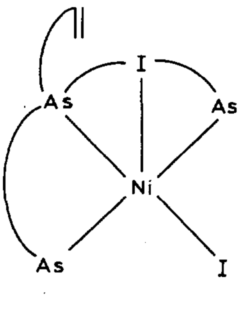
Nickel(II) complexes

Nickel(II) complexes of tasol. Reaction of nickel(II) halides with tasol in alcohol solvents led to the formation of deeply coloured pentacoordinate complexes of formula $[NiX(tasol)]^+$ (X = Cl, Br) and $[NiI_2(tasol)]$; in addition, some dinuclear species were also isolated (see Experimental) using metal/ligand ratios other than 1/1 (Table 2).

The $NiBr_2(tasol)$ complex is a 1 : 1 electrolyte in dichloromethane and nitromethane, dilution studies confirming this for the latter solvent. There are two formulations consistent with this electrolyte type, viz.: the four-coordinate $[NiBrAs_3]^+$ or the pentacoordinate $[NiBrAs_3ol]^+$. The strong absorption in the electronic spectrum at 16400 cm^{-1} is inconsistent with a planar or a tetrahedral



(V)



(VI)

TABLE 2

ANALYTICAL AND CONDUCTOMETRIC DATA FOR THE NICKEL(II) COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))			Λ_M [a]	Slope [b]
		C	H	Hal		
[NiBr(tasol)]Br	Deep blue	26.8 (26.2)	4.4 (4.7)	Br 25.2 (24.9)	89	210
$[NiI_2(tasol)]\cdot EtOH$	Green black	24.9 (24.6)	4.6 (4.8)	I 32.3 (32.5)	14	
$[NiCl(tasol)]ClO_4$	Deep blue	27.3 (27.3)	4.6 (5.0)		81	195
$[NiBr(tasol)]ClO_4\cdot CH_2Cl_2$	Deep blue	24.1 (24.1)	4.4 (4.4)		81	202
$[NiCl(tasol)]BPh_4\cdot CHCl_3$	Dark blue	49.1 (48.9)	5.7 (5.5)		69	241
$[NiCl(tasol)]BPh_4\cdot CH_2Cl_2$	Dark blue	49.8 (49.6)	5.9 (5.8)		69	238
$[NiBr(tasol)]BPh_4\cdot CH_2Cl_2$	Dark blue	49.0 (48.8)	6.0 (5.7)		71	253
$[NiCl(tasol)(H_2O)]ClO_4$	Red purple	25.9 (26.4)	5.0 (5.2)	Cl 4.4 (4.4)	78	231
$[Ni_2(tasol)_3(H_2O)](ClO_4)_4$	Violet	27.9 (27.9)	5.4 (5.3)		306	3100
$[Ni_2I_3(tasol)_3(H_2O)]ClO_4$	Black	23.0 (23.0)	4.8 (4.4)		77	
$[NiCl(dasdol)_2]Cl$	Deep blue			Cl 19.0 (18.9)	83	
$[NiBr(dasdol)_2]Br$	Deep blue			Br 18.3 (18.1)	85	
$[NiI(dasdol)_2]I$	Dark green			I 26.4 (26.0)	77	
$[NiCl(dasdol)_2]BPh_4$	Dark blue	55.9 (55.7)	6.3 (6.7)	Cl 3.4 (3.2)	79	
$[NiBr(dasdol)_2]BPh_4$	Dark blue	52.9 (53.5)	5.9 (6.5)	Br 7.3 (7.1)	82	

[a] Molar conductance ($cm^2\ ohm^{-1}\ mol^{-1}$) in 10^{-3} M solution in nitromethane. [b] Slope of plot of $\Lambda_0 - \Lambda_e$ vs. $\sqrt{C}$ in nitromethane.

structure, nor is it comparable to the square pyramidal structure of $[NiBr_2(trias)]$ (trias = bis(3-dimethylarsinopropyl)arsine) [24], but closely resembles that of the trigonal bipyramidal $[NiBr(tas)]^+$ cation (tas = tris(3-dimethylarsinopropyl)arsine) [25]. The solid reflectance spectrum is similar and thus the complex is assigned a structure containing coordinated olefin, V. Further evidence for this is found in the infrared spectrum, which exhibits a new band at 1590 (Nujol) or 1580 cm^{-1} (dichloromethane). A medium absorption at 230 cm^{-1} is in the range characteristic of ν(Ni–Br) for this type of complex [26].

In contrast the NiI_2(tasol) complex is essentially non-conducting in fresh solutions in organic solvents (though conductivity slowly rises with time). The electronic spectrum of the $[NiI_2(tasol)]$ complex (Table 3) closely resembles that of $[NiI_2(trias)]$, which is square pyramidal [24]. Moreover, infrared spectra of $[NiI_2(tasol)]$ in the solid state and in dichloromethane exhibit ν(C=C) at 1635 cm^{-1} assignable to uncoordinated olefin. Accordingly, NiI_2(tasol) is assigned structure VI.

TABLE 3

ELECTRONIC SPECTRA OF THE NICKEL(II) COMPLEXES (cm^{-1})

	Solution[a]		Solid reflectance
[NiBr(tasol)]Br	14800(sh)	(620)	14100
	16400	(890)	15700
	21400(sh)	(210)	20700
	28000(sh)	(1260)	
	29500(sh)	(1800)	
	35100(sh)	(9700)	
$[NiI_2(tasol)]\cdot EtOH$	15000(sh)	(855)	
	16500	(920)	
	24500(sh)	(1850)	
	32800	(10500)	
	36400	(9600)	
	42000	(11550)	
$[NiCl(tasol)]ClO_4$	14500(sh)	(680)	14000
	16250	(870)	15900
	21100(sh)	(375)	
	26600	(640)	26700(sh)
$[NiBr(tasol)]ClO_4\cdot CH_2Cl_2$	14200(sh)	(660)	13800
	15900	(1130)	15700
	21000(sh)	(410)	
	26450	(770)	26300(sh)
$[NiCl(tasol)]BPh_4\cdot CHCl_3$	14700(sh)	(825)	14100
	16700	(1025)	16400
	22050(sh)	(420)	20700(sh)
	27200	(370)	26800(sh)
$[NiBr(tasol)]BPh_4\cdot CH_2Cl_2$	14400	(1175)	14150
	16200	(1550)	20400(sh)
	26800	(410)	
$[NiCl(tasol)(H_2O)]ClO_4$	13000	(250)	
	22500	(1650)	
	28000(sh)	(1140)	
$[Ni_2I_3(tasol)_2(H_2O)]ClO_4$	13700		13500
	17100		17600
	23400(sh)		21200
$[Ni_2(tasol)_3(H_2O)](ClO_4)_4$	17500(sh)	(800)[c]	16700(sh)
	18800	(1690)	18500
	27700(sh)	(1280)	23000(sh)
$[NiCl(dasdol)_2]Cl$	17500(sh)	(540)[b]	
	19530	(610)	19100
	29000(sh)	(3200)	25050(sh)
	37000(sh)	(8200)	
	42300	(15400)	
$[NiBr(dasdol)_2]Br$	18800	(680)[b]	18500
	26000(sh)	(1950)	23500
$[NiI(dasdol)_2]I$	17700	(750)[b]	
	25800(sh)	(1090)	
	33200	(7200)	
	36100(sh)	(11200)	
	40700	(16400)	
$[NiI(dasdol_2)]BPh_4$	14850	(170)[b]	13700(sh)
	17100	(450)	17050
	25800	(1460)	27050(sh)

[a] Extinction coefficient in parentheses. [b] In nitromethane. [c] In dichloromethane.

Both NiX_2(tasol) (X = Br, I) exhibit weak temperature independent paramagnetism, sufficient to render the ^1H NMR spectra uninterpretable.

Addition of $NaClO_4$ or $NaBPh_4$ to ethanolic solutions of NiX_2(tasol) (X = Cl,Br) precipitated the deep blue [NiX(tasol)]Y (Y = ClO_4, BPh_4) complexes (Table 2). Conductivity measurements are consistent with 1 : 1 electrolytes in dichloromethane, and dilution studies in nitromethane confirm this electrolyte type. The reaction of $NaClO_4$ or $NaBPh_4$ with NiI_2(tasol) gave very different results (see below).

The electronic spectra (Fig. 1) of the [NiX(tasol)]Y are consistent with trigonal bipyramidal geometry. Comparing the spectra with those of the $[NiX(tas)]^+$ (X = Cl, Br) [25] show only a slight shift to lower energy of the main absorption ca. 16000 cm^{-1} on changing the donor set from $[NiXAs_4]^+$ to $[NiXAs_3(olefin)]^+$. In both the mull and dichloromethane solution infrared spectra of the [NiX(tasol)]Y (X = Cl, Br; Y = ClO_4, BPh_4) the ν(C=C) band due to free tasol was absent and for the perchlorate species a weak, sharp band at 1590 (X = Cl) and 1580 cm^{-1} (X = Br) is present, assignable to coordinated olefin (bands due to BPh_4^- masked these absorptions in the tetraphenylborate complexes). The ν(Ni–Cl) occurs at 350 and ν(Ni–Br) at 230 cm^{-1}. The perchlorate bands at 1100 and 620 cm^{-1} are unsplit, evidence of ionic perchlorate [27].

We have examined the reactivity of the coordinated olefin group. When the blue

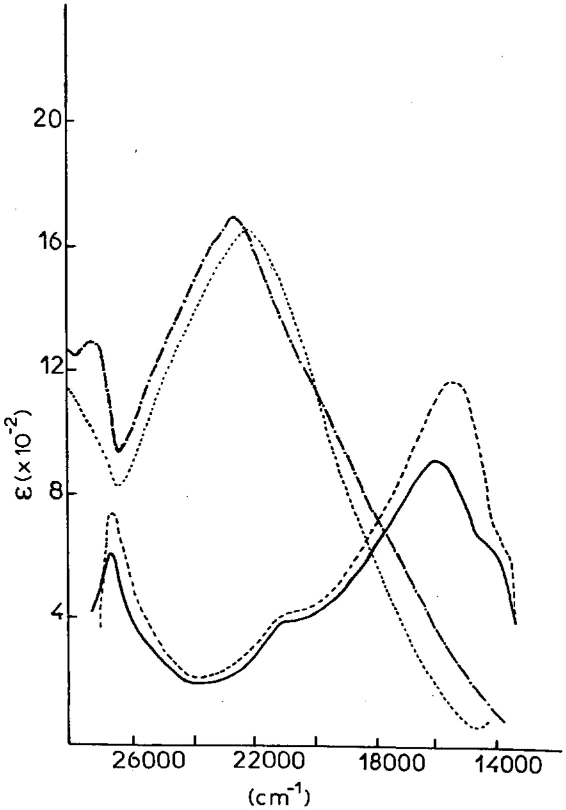


Fig. 1. Electronic spectra of the tasol complexes; ——— $[NiCl(tasol)]ClO_4$, — — — $[NiBr(tasol)]ClO_4$, ------ $[NiCl(tasol)(H_2O)]ClO_4$, -·-·- $[Ni_2(tasol)_3(H_2O)]ClO_4$.

$[NiCl(tasol)]ClO_4$ was stirred in an ethanol/water medium, the solution rapidly became purple. Removal of the solvent yielded the $[NiCl(tasol)(H_2O)]ClO_4$ complex (Table 2) which is a 1 : 1 conductor in dichloromethane and nitromethane. There are new infrared bands in this complex which are not present in the starting material, viz. a strong broad absorption at ca. 3450, ν(OH), and a medium band at 1625 cm^{-1}, $\delta(OH_2)$. No band at 1590 cm^{-1} is present, but a band assignable to free olefin occurs at 1640 cm^{-1}. The available evidence thus indicates the replacement of the coordinated olefin by a water molecule. The electronic spectra (Fig. 1, Table 3) suggests that $[NiCl(tasol)(H_2O)]ClO_4$ has an essentially square pyramidal structure about the nickel atom.

When ethanolic/dichloromethane solutions of $NaBPh_4$ and $[NiI_2(tasol)]$ are mixed, a dark green solid is obtained, but analytical data indicated that the reaction was non-reproducible. For the insoluble $[Ni_2I_3(tasol)_2(H_2O)]ClO_4$, (IR 3500, 1620 cm^{-1} (H_2O) and free olefin 1640 cm^{-1} [27]) the electronic reflectance spectrum (Fig. 1) is reminiscent of an essentially square pyramidal molecule, structure IV, such a structure explaining the considerable assymmetry of the electronic spectra bands. It has been shown that similar dimeric species are produced employing the ligand bis(*o*-dimethylarsinophenyl)methylarsine [28].

The reaction of NiI_2(tasol) with ClO_4^- to yield a polynuclear species rather than to lead to the pentacoordinate $[NiI(tasol)]^-$, containing coordinated olefin, contrasts with the stability of the $[NiX(tasol)]^+$ (X = Cl, Br) species. Clearly the nature of the halide has a crucial effect on promotion of nickel–olefin bonding.

Direct reaction of tasol with $Ni(H_2O)_6(ClO_4)_2$ in ethanol produced the immediate precipitation of a bright purple solid, $[Ni_2(tasol)_3(H_2O)](ClO_4)_4$, and this material was produced irrespective of the mole ratio of reactants. A complex of similar stoichiometry has been reported for the triarsine [28], and both complexes have almost identical electronic spectra (Table 3). The presence of water is confirmed by the infrared spectrum, and only coordinated perchlorate groups are present; a band at 1650 cm^{-1} is assigned to free olefin groups. The complex is readily soluble in nitromethane and the resulting solution is stable for > 1 h. The molar conductance of a 10^{-3} *M* solution is 306 cm^2 ohm^{-1} mol^{-1}, in excellent agreement for a 1 : 4 electrolyte. A plot of $\Lambda_0 - \Lambda_e$ vs. $\sqrt{C}$ in the 10^{-3}–5×10^{-4} *M* region gives a slope of 3100. Little literature data is available for comparison, but the high numerical value is a reasonable one. Addition of excess $NaBPh_4$ to this complex in ethanol leads to no change in the electronic spectrum, suggesting that ClO_4^- groups can be exchanged without the $[Ni_2(tasol)_3(H_2O)]^{4+}$ chromophore undergoing any rearrangement despite the size of the new counter anion.

The $[NiX(tasol)]^+$ (X = Cl, Br) cations thus contain a coordinated olefin group, the ν(C=C) moving ca. 60 cm^{-1} to lower energy from that in the free ligand; this is similar to that observed in, for example, silver (I)–olefin complexes [29].

Nickel(II) complexes of dasdol. Addition of dasdol to nickel(II) halides in anhydrous ethanol gives deeply coloured solutions, from which can be obtained $NiX_2(dasdol)_2$ (Table 2) on concentration. The reaction mixtures are very susceptible to moisture. Irrespective of ligand: nickel ratios, only $NiX_2(dasdol)_2$ complexes could be isolated. The complexes are 1 : 1 electrolytes in dichloromethane and *N*,*N'*-dimethylformamide, but in the latter the conductivities slowly increased until the values approached those of 1 : 2 species, and presumably solvolysis occurs to produce $[Ni(dasdol)_2(DMF)]^{2+}$.

The mull and dichloromethane solution infrared spectra show no evidence for coordinated olefin but all $[NiX(dasdol)_2]X$ complexes show evidence for free olefin at 1635 cm^{-1}. The electronic spectra are consistent with pentacoordinate square pyramidal species containing the $[NiXAs_4]^+$ chromophore, the main absorption moving to lower energy in the order Cl > Br > I (Table 3). The spectra are similar to other $[NiXAs_4]^+$ complexes reported to have a square pyramidal structure [30,31].

Our inability to isolate planar complexes $[NiX_2(dasdol)]$, irrespective of using excess NiX_2 in the preparative reactions parallels the chemistry of diars, o-$C_6H_4(AsMe_2)_2$ [32].

We were able to isolate $[NiX(dasdol)_2]BPh_4$ by reaction of $[NiX(dasdol)_2]X$ with $NaBPh_4$ in ethanol (Table 2). The complex cation in both types of complex are identical, as evidenced by electronic spectra (Table 3).

Nickel(II) complexes of astol. We were unable to observe any reaction between nickel(II) salts and the arsinetriolefin ligand, tris(but-3-enyl)-arsine.

Conclusion

We have studied the reaction of nickel(II) salts with three ligands with trigonal symmetry and with the donor sets As_3ol, As_2ol_2 and $Asol_3$, and find that complexes can be isolated with the first two ligands to yield trigonal bipyramidal $[NiX(tasol)]^+$ (X = Cl, Br) and square pyramidal $[NiX(dasdol)_2]^+$ (X = Cl, Br, I) containing the donor sets $[NiXAs_3ol]$ and $[NiXAs_4]$, respectively. In addition, the tasol ligand, but not the dasdol ligand, formed polynuclear complexes. In further comparing the reactivity of these three potentially quadridentate ligands, it may be concluded: (i) that the expected "chelate effect" does not obtained, inasmuch as of these three ligands with trigonal symmetry, only one acts as a tripod ligand promoting pentacoordinate trigonal bipyramidal $[NiX(ligand)]^+$ complexes, and (ii) that the promotion of nickel(II)–olefin coordination with tasol but not with dasdol would appear to indicate that, in the absence of the chelate effect of all three trigonally symmetrical ligands, it is the presence of the two arsenic atoms in the plane of the molecule which so modified the relatively hard nickel(II) acid so that it can accept an olefin donor. The formation of a stable nickel(II)–olefin bond is even more remarkable in this system, as it is known that the stability of olefin complexes decreases as the overall positive charge on the complex increases. (iii) Regarding the effect of X in NiX_2 in the reaction with olefin, it is seen that the nickel(II) salts act in a similar manner to platinum(II) salts towards olefin systems, i.e. the tendency for the halide to displace the metal–olefin bond being I ≫ Br > Cl [14,33].

Experimental

Preparation of but-3-enylbis(3-dimethylarsinopropyl)arsine (tasol)

Stage 1. Synthesis of 3-chloropropyldimethylarsine. $Cl(CH_2)_3AsMe_2$, b.p. 44°C/0.5 mmHg, was prepared in good yield by slight modifications of published routes [20,21,25].

Stage 2. Synthesis of 2-chloroethyldichloroarsine. $Cl(CH_2)_3AsMe_2$, b.p. 65°C/1.0 mmHg, was isolated from a similar reaction procedure, but in a reduced yield (11% based on 2-chloroethanol starting material) mostly as a pale liquid contaminated with iodine, the final distillation fractions being very dark indeed. Redistillation did not remove the iodine. (*Warning*: This material is a potent vesicant.)

Stage 3. Synthesis of 2-chloroethylbis(3-dimethylarsinopropyl)arsine (trias). A two litre three-necked flask was equipped with a 250 ml dropping funnel with a pressure-equalizing side-arm, a reflux condenser, a mechanical stirrer and a nitrogen inlet. The flask was charged with 2-chloroethyldichloroarsine (22 g, 0.1 mol) in dry ether (400 cm^3) and the mixture cooled to about -30°C by a cardice/acetone bath. Grignard reagent resulting from the reaction of Mg with 3-chloropropyldimethylarsine (0.25 mol in 100 cm^3 THF) was added to the mixture dropwise with vigorous stirring. Initially, a white precipitate was formed which turned yellow-orange towards the end of the addition. The mixture was then refluxed for 1 h, cooled to 0°C, and then hydrolyzed with aqueous ammonium chloride solution (35 g in 250 cm^3 water). The upper ethereal layer was separated and dried over anhydrous sodium sulphate. The ether was stripped leaving a yellow oil. The crude product was heated at 120°C under a pressure of 0.2 mmHg for 2 h to remove all volatiles. The remaining oil was dried over molecular sieves to remove the last traces of water. The oil is very air sensitive and was stored under an atmosphere of nitrogen. The product began to decompose at 165°C at 0.1 mmHg before distillation took place and was used without further purification. Yield was 25 g, 60% based on 2-chloroethyldichloroarsine.

Stage 4. Synthesis of but-3-enylbis(3-dimethylarisonopropyl)arsine (tasol) A flask (500 cm^3) was charged with magnesium turnings (5.0 g, 0.21 mol) and THF. A mixture of vinyl bromide (25 g, 0.25 mol) and THF (50 cm^3) was cooled to 0°C, and added at a rate sufficient to maintain a vigorous reaction. When the addition was complete, the mixture was refluxed for 30 min, and then allowed to cool to room temperature.

2-Chloroethylbis(3-dimethylarsinopropyl)arsine (15 g, 0.034 mol) in THF (50 cm^3) was added to the stirred Grignard reagent at 0°C. A white precipitate quickly formed and persisted throughout the addition. When the addition was complete, the mixture was refluxed for 2 h. The mixture was hydrolyzed with aqueous ammonium chloride (25 g in 200 cm^3 of water) at 0°C and the two phase mixture separated. The lower aqueous layer was washed twice with ether (100 cm^3 portions) and the washings added to the upper ethereal layer. The ethereal layer was dried over anhydrous sodium sulphate and the ether removed at room temperature and a pressure of 2 mmHg. The residual yellow oil was heated to 120°C at 0.1 mmHg pressure for 2 h to remove volatiles and stored under nitrogen over molecular sieves.

The crude product decomposed at about 150°C before distilling and consequently further purification was not possible. The infrared spectrum of the oil was consistent with the presence of an olefin group, and the NMR spectrum could similarly be assigned to the compound being the tasol ligand. It proved impossible to remove all traces of the triarsine precursor (identified by a strong broad absorption in the IR at 750 cm^{-1}) but NMR indicated that the impurities were less than 5%.

The tasol ligand was obtained as a pale yellow oil which proved very air sensitive. The principal oxidation product was again a white solid. Yield of the crude product was 10 g; 65% based on the triarsine precursor.

Preparation of 3-dimethylarsinopropylbis(but-3-enyl)arsine (dasdol)

Stage 1. Synthesis of 3-chloropropylbis(but-3-enyl)arsine. A Grignard reagent of 4-chlorobut-1-ene (29 g, 0.23 mol) was prepared. 3-Chloropropyldichloroarsine (30 g, 0.134 mol) in dry ether (200 cm^3) was transferred to a 2-l three-necked flask which was equipped with a 250 ml dropping funnel with a pressure equalizing sidearm, a mechanical stirrer, a reflux condenser and a nitrogen inlet. The solution was cooled to about −30°C by means of a cardice/acetone bath and the temperature maintained in this region. The Grignard reagent was added dropwise to the cooled solution with vigorous stirring. A heavy white precipitate quickly formed and persisted throughout the reaction. When the addition was complete, the mixture was refluxed for 30 min, cooled to 0°C and carefully hydrolyzed with aqueous ammonium chloride (25 g in 300 cm^3 of water). The resulting two-phase mixture consisted of a pale yellow upper phase and a grey heavier lower phase. The upper phase was separated, the lower phase washed twice with ether (100 cm^3 portions) and the combined ether phases dried over anhydrous sodium sulphate. The ether removed under 2 mmHg pressure at room temperature, leaving a pale yellow oil. Vacuum distillation gave a colourless, air-sensitive, oil, b.p. 88–90°C at 0.4 mmHg. The yield of pure product was 25 g; 51% based on 4-chlorobut-1-ene.

The infrared spectrum of the neat liquid showed absorptions in the 3080, 1645, 990 and 915 cm^{-1} regions (which is indicative of the presence of the $CH_2=CHR$ group) and a broad band at 750 cm^{-1} i.e. ν(C–Cl).

3-Chloropropylbis(but-3-enyl)arsine (15 g, 0.058 mol) in dry ether (150 cm^3) was syringed into the flask under nitrogen. An ammonia solution of sodium dimethylarsenide (0.07 mol) was added dropwise to the stirred solution; the flask was warmed to prevent ice forming on the surface of the flask as ammonia evaporated. The colour was instantly discharged upon reaching the ethereal solution. The solution in the flask became pale yellow and the colouration persisted throughout the addition.

The mixture was allowed to warm up to room temperature and refluxed for 30 min to complete the reaction. The slight red colouration persisted throughout the period of refluxing. As the ammonia evaporated, a fine white precipitate formed, the solution being a pale red-orange throughout. The mixture was carefully hydrolyzed with deoxygenated water (50 cm^3), a two-phase mixture remaining. The upper pale yellow ethereal layer was separated and the lower aqueous layer washed twice with ether (100 cm^3 portions). The combined ether phases were dried over sodium sulphate.

The ether was removed to leave a residual pale yellow oil which was distilled under reduced pressure. A very small fraction corresponding to the unreacted 3-chloropropylbis(but-3-enyl)arsine was collected, b.p. 85°C/0.1 mmHg. The product was collected as a colourless oil, b.p. 125–130°C/0.1 mmHg. The distillation was accompanied by some pyrolysis of the product.

The product was obtained as a colourless oil, yield 13 g, 67%. The product is air sensitive and was stored under nitrogen over molecular sieves.

Preparation of [NiX(tasol)]X (X = Br, I)

These complexes were prepared by the same route, which is exemplified by the preparation of the bromo complex.

Nickel(II) bromide · $3H_2O$ (0.8 g, 2.8 mmol) was dissolved in gently refluxing ethanol (20 cm^3) under nitrogen. The ligand tasol (1.2 g, 2.7 mmol) in ethanol (10 cm^3) was added to the stirred solution over 5 min, and the pale green solution rapidly turned deep blue and was refluxed for a further 20 min. The ethanolic solution was concentrated and cooled to 0°C in an ice bath. Careful addition of n-butanol and cooling to $-75°C$ precipitated the deep blue solid, which was washed with cold butanol (0°C) and ether and dried in vacuo to yield 0.86 g, 50%.

All attempts to prepare the analogous chloro complex proved unsuccessful. The same intensely deep blue solutions were observed but no pure complex could be isolated from the reaction mixture.

Preparation of [NiX(tasol)]ClO$_4$ (X = Cl, Br)

These complexes were prepared by the same route which is exemplified by the preparation of [NiCl(tasol)](ClO$_4$).

A solution of "NiClClO$_4$" was prepared by the method of Dubois and Meek [34]. Nickel(II) chloride · 6H_2O (0.24 g, 0.1 mmol) and nickel(II) perchlorate · 6H_2O (0.36 g, 0.01 mmol) were mixed with 2,2-dimethoxypropane (20 cm^3) and the solution refluxed for 30 min. Ethanol (15 cm^3) was added to the mixture and the solution refluxed under nitrogen for 10 min. The ligand tasol (0.9 g, 1.9 mmol) in ethanol (10 cm^3) was added over 5 min to the stirred solution, which rapidly became deep blue. On cooling and concentrating the solution, a deep blue solid was precipitated.

Preparation of [Ni$_2$I$_3$(tasol)(H$_2$O)]ClO$_4$

The complex was prepared in the same manner as the [Ni(tasol)Cl](ClO$_4$) complex. The product was obtained as a very dark green powder in 80% yield and investigations established this complex as [Ni$_2$(tasol)$_2$I$_3$(H$_2$O)](ClO$_4$). No simple [Ni(tasol)I](ClO$_4$) complex could be isolated.

Preparation of [Ni$_2$(tasol)$_3$(H$_2$O)](ClO$_4$)$_4$

Nickel(II) perchlorate · 6H_2O (0.8 g, 2.2 mmol) was dissolved in gently refluxing ethanol (20 cm^3) under nitrogen. The pale green solution was stirred and the ligand tasol (0.9 g, 2.2 mmol) in ethanol (10 cm^3) was added. The solution became purple almost immediately and a purple solid began to precipitate, which was filtered from the cherry red solution, collected on a sinter, washed with hot ethanol and ether, and dried under vacuo.

The reaction was repeated with a molar ratio of 1/2 of nickel perchlorate to tasol. A similar bright purple solid was isolated and investigations showed that this complex is also [Ni$_2$(tasol)$_3$(H$_2$O)](ClO$_4$)$_4$.

Preparation of [NiCl(tasol)(H$_2$O)(ClO$_4$)

The complex [NiCl(tasol)](ClO$_4$) (0.25 g, 0.4 mmol) was dissolved in an ethanol/water mixture (10/1 by volume) and the mixture refluxed for 30 min. The colour of the solution gradually changed from deep blue to red-purple and concentration of the solution precipitated a red-purple solid, which was collected, washed rapidly with ether and dried to yield 0.22 g, 86%. The complex is exceedingly hygroscopic and was stored in a dessicator.

Preparation of [Ni(tasol)X]BPh$_4$ (X = Cl, Br)

These complexes were prepared by the addition of an ethanolic solution of sodium tetraphenylborate to a similar solution of Ni(tasol)X$_2$ in the appropriate 1/1 molar ratio. The complexes were isolated and recrystallized from a dichloromethane/ethanol mixture in 85–90% yield.

The addition of sodium tetraphenylborate to the Na(tasol)I_2 complex gave a dark green solid that could not be obtained pure.

Nickel(II) complexes of dasdol

Complexes of the type [NiX$(dasdol)_2$]X (X = Cl, Br, I) were prepared by an identical route. The preparation of [NiBr$(dasdol)_2$]Br will serve as an example.

Anhydrous nickel(II) bromide (0.20 g, 0.68 mmol) was dissolved in anhydrous ethanol (20 cm^3) and the pale green solution refluxed for 30 min. A solution of dasdol (0.5 g, 1.51 mmol) in anhydrous ethanol (5 cm^3) refluxed for a further 15 min. The solution was evaporated to dryness and butanol (20 cm^3) added and stirred at −70°C. The blue solid resulting was rapidly collected on a pre-cooled filter stick under nitrogen and transferred to a number of small weighed sample tubes. Total yield 0.5 g, 75%.

The chloro species was isolated as a deep blue solid, the iodo complex as a dark green solid. The three complexes are extremely hygroscopic and were stored in vacuo over phosphorus pentoxide.

Preparation of the [NiX$(dasdol)_2$]BPh_4 (X = Cl, Br)

These complexes were prepared by the addition of $NaBPh_4$ to an ethanolic solution of the appropriate [Ni(dasdol)X]X species in a 1/1 molar ratio. The ethanol was removed under vacuum and the oily mixture extracted with dichloromethane. The solution was filtered under nitrogen and the solvent again removed under nitrogen. Solid phases were isolated by an analogous technique to that used for the [NiX$(dasdol)_2$]X complexes.

Physical measurements were obtained as previously described [14].

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