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Novel rhodate and iridate complexes containing C,N chelating arylamine ligand systems *

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Abstract

The synthesis is described of a series of new iridate and rhodate complexes Li(L-*C*,*N*)$_2$M(cod) (M = Rh, Ir; cod = cycloocta-1,5-diene) containing the *ortho*-chelating, mono-anionic, arylamine ligands L = $C_6H_4CH_2NR_2$-2 (R = Me, Et), $C_6H_3CH_2NMe_2$-2-Me-5, $C_6H_4CH(Me)NMe_2$-(*R*)-2 or $C_6H_4CH_2NMe(^tBu)$-2. The synthetic procedure for the -ate complexes from $[MCl(cod)]_2$ depends on the solubility of the starting aryllithium compound in benzene—an indirect effect of the bulky organic group on the N-donor atom. All the -ate complexes are formed diastereoselectively (and in the case of $C_6H_4CH(Me)NMe_2$-(*R*)-2, enantioselectively). ^1H and ^{13}C NMR spectroscopies show the -ate complexes to be monomeric, heterobimetallic species. The ^{13}C NMR data show clearly that C_{ipso} is bridging between the late transition metal and the lithium centre. Consequently, this C_{ipso} atom is chiral, and its configuration is stabilized by intramolecular coordination of the N-donor atom of the *ortho*-amine substituent. The -ate complexes are fluxional with differences in fluxionality (which involve N-dissociation/association, pyramidal inversion at N and rotation around the C_{benzyl}–N bond) that can be attributed to differences in the bulk of the groups on the nitrogen atom.

1. Introduction

Over the past decade there has been a growing interest in heterobimetallic complexes containing a combination of an alkali and a late transition metal [1]. These metallate complexes are not only useful reagents in organic chemistry [2] but may also act as mild alkylating agents towards transition metal halide complexes [1j] or serve as useful precursors for the preparation of other types of heterobimetallic complexes [3]. In particular such complexes containing both an early and a late transition metal centre currently attract much attention, because they show a combination of the characteristic reactivities of both centres in catalysis [4].

Metallate complexes of the cobalt triad metals containing bridging alkyl or aryl groups have been reported [1i,j,5]. In these complexes the square-planar geometry of the late transition metal is completed with π-acid ligands such as phosphines or olefins, and the tetrahedral geometry of the lithium atom is completed with coordinating molecules such as tetrahydrofuran (thf), diethyl ether, or tetramethylethylenediamine (tmeda). However, when the latter are not present, dimerization of the -ate complex may occur, though this process is blocked when bulky phosphine ligands are coordinated to the rhodium or iridium centres. The use of sterically bulky ligand systems has long been recognized as a means of changing the behaviour of organometallic complexes [6], but so far most of this research has been concentrated on phosphine ligands; only recently have reports on the steric influences of nitrogen ligands appeared [7].

We recently initiated studies directed towards elucidating the influence of bulky nitrogen ligand systems on the reactivity of cyclometallated arylamine complexes of the late transition metals [7a,b,d,g,h]. In the course of this research, we found that using an excess of an arylamine lithium compound (LiL, L = mono-anionic C,N bidentate coordinating ligand) in metathesis reactions that were designed to afford neutral

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square-planar rhodium and iridium complexes [ML-(cod)] (cod = cycloocta-1,5-diene), another type of complex $[LiL_2M(cod)]$, *i.e.* an -ate complex, was formed. We describe below the syntheses and structural characterization of these rhodate and iridate complexes, whose dimerization is hindered by intramolecular coordination of the *ortho*-amine substituent to the Li atom. For these species in solution the fluxionality is found to decrease with increasing bulk of the N-donor ligand.

2. Experimental details

Syntheses were carried out by use of standard Schlenk techniques under purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. The compounds $[RhCl(cod)]_2$ [8], $[IrCl(cod)]_2$ [7g], $Li(C_6H_4CH_2NRR'\text{-}2\text{-}C,N)$ (R = R' = Me [9]; R = R' = Et [7h]; R = Me, R' = ^{t}Bu [7h], $Li(C_6H_4CH(Me)\text{-}NMe_2\text{-}(R)\text{-}2\text{-}C,N)$ (starting from commercially available $(R)\text{-}C_6H_5CH(Me)NH_2$ with an e.e. of 96%) [10] $Li(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5\text{-}C,N)$ [9], $Li(1\text{-}C_{10}H_6\text{-}NMe_2\text{-}8\text{-}C,N)(OEt_2)$ [9], $Rh(C_6H_4CH_2NRR'\text{-}2\text{-}C,N)\text{-}(cod)$ (R = R' = Et; R = Me, R' = ^{t}Bu) [7h] and $Ir(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(cod)$ [7g] were prepared by published methods. ^1H, ^{13}C and 2D NMR spectra were recorded on Bruker AC 200 and AC 300 spectrometers, by use of standard pulse sequences for the ^{13}C, ^1H COSY measurements [11]. For the low temperature NMR experiments toluene-d_8 was used as solvent.

2.1. Synthesis of $Rh(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)\text{-}(cod)$ (1)

A solution of $Li(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)$ (0.08 g, 0.5 mmol) in C_6H_6 (5 ml) was added during 30 min to a solution of $[RhCl(cod)]_2$ (0.12 g, 0.25 mmol) in C_6H_6 (15 ml). After 2.5 h stirring, the suspension was centrifuged and the supernatant solution decanted. The solid residue was extracted with C_6H_6 (10 ml) and the combined extract and supernatant liquid were evaporated *in vacuo* to leave an oily residue. Upon addition of hexane (5 ml) a solid precipitated out, and this was washed with hexane (5 ml) and dried *in vacuo* to afford **1** as an orange powder (0.17 g, 97% yield).

^1H NMR (C_6D_6, 24°C): δ 7.3 (d, 1H, Ar-*H*(6), $^3J(^1H,^1H) = 7$ Hz), 7.13 (m, 3H, Ar-*H*(3,4,5)), 4.29 (br, 2H, =C*H*), 4.03 (m, 1H, =C*H*), 3.86 (m, 1H, =C*H*), 3.11 (qd, 1H, Ar-C*H*(Me)-N, $^3J(^1H,^1H) = 7$ Hz, $^3J(^{103}Rh,^1H) = 1.5$ Hz), 2.89 (s, 3H, -NCH_3), 1.95-2.55 (m, 6H, -CH_2-), 1.85 (s, 3H, -NCH_3), 1.7-1.9 (m, 2H, -CH_2-), 1.39 (d, 3H, Ar-CH(CH_3)-N, $^3J(^1H,^1H) = 7$ Hz).

^{13}C NMR (C_6D_6, 24°C): δ 164.2 (C_{ipso}, $^1J(^{103}Rh,^{13}C) = 36.6$ Hz), 156.2 (Ar-*C*(2)), 133.9 (Ar-*C*(6), $^2J(^{103}Rh,^{13}C) = 1.4$ Hz), 124.9 (Ar-*C*(3), $^3J(^{103}Rh,^{13}C) = 1.2$ Hz), 124.3 (Ar-*C*(5)), 121.9 (Ar-*C*(4)), 89.3 (=*C*H, $J(^{103}Rh,^{13}C) = 6.9$ Hz), 89.2 (=*C*H, $J(^{103}Rh,^{13}C) = 7.5$ Hz), 76.1 (Ar-*C*H(Me)-N), 72.4 (=*C*H, $J(^{103}Rh,^{13}C) = 15.3$ Hz), 71.5 (=*C*H, $J(^{103}Rh,^{13}C) = 14.5$ Hz), 49.7 (-N*C*H_3), 44.8 (-N*C*H_3), 33.0 (-*C*H_2-), 30.9 (-*C*H_2-), 30.7 (-*C*H_2-), 29.4 (-*C*H_2-), 25.6 (Ar-CH(*C*H_3)-N).

Anal. Found: C 60.26; H 7.34; N 3.96. $C_{18}H_{26}NRh$ calcd.: C, 60.17; H, 7.29; N, 3.90%.

2.2. Synthesis of $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2Rh(cod)$ (2)

A suspension of $[RhCl(cod)]_2$ (0.09 g, 0.18 mmol) and $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$ (0.1 g, 0.7 mmol) in C_6H_6 (15 ml) was agitated for 3.5 h in an ultrasonic bath. The resulting suspension was centrifuged (to remove LiCl), the clear supernatant solution was decanted under nitrogen, and evaporated to dryness *in vacuo*. The residue was triturated with hexane (3 × 10 ml), then dried *in vacuo* to give **2** as a yellow-orange powder in 90% yield.

2.3. Syntheses of $Li(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)_2Rh(cod)$ ($R^1 = CH_2NMe_2$, $R^2 = Me$ (3); $R^1 = CH_2NEt_2$, $R^2 = H$ (4); $R^1 = CH(Me)NMe_2$, $R^2 = H$ (5); $R^1 = CH_2NMe(^tBu)$, $R^2 = H$ (6))

A solution of $Li(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)$ (*ca.* 5 equivalents) in C_6H_6 (15 ml) was added during 30 min to a solution of $[RhCl(cod)]_2$ (*ca.* 0.3 mmol) in C_6H_6 (10 ml). The resulting suspension was stirred for another 3 h and then centrifuged to remove the precipitated LiCl. The clear supernatant solution was decanted under nitrogen and evaporated to dryness *in vacuo*. The residue was triturated with pentane or hexane (5 × 6 ml) then dried *in vacuo* to give the rhodate complexes $Li(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5\text{-}C,N)_2Rh(cod)$ (**3**), $Li(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)_2Rh(cod)$ (**4**), $Li(C_6H_4\text{-}CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)_2Rh(cod)$ (**5**) and $Li(C_6H_4\text{-}CH_2NMe(^tBu)\text{-}2\text{-}C,N)_2Rh(cod)$ (**6**) as orange powders in quantitative yield.

Alternatively, these compounds may be obtained by mixing the organolithium compound and the corresponding organorhodium compound, *i.e.* $Rh(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)(cod)$, in a 1:1 molar ratio in benzene.

Mol. weight (cryoscopy in benzene) for $Li(C_6H_4\text{-}CH_2NEt_2\text{-}2\text{-}C,N)_2Rh(cod)$ (**4**); 406 g mol^{-1} (0.06 mol l^{-1}), calcd. for monomeric **4**; 542 g mol^{-1}.

2.4. Syntheses of $Li(C_6H_4R\text{-}2\text{-}C,N)_2Ir(cod)$ ($R = CH_2NEt_2$ (7); $R = CH_2NMe(^tBu)$ (8))

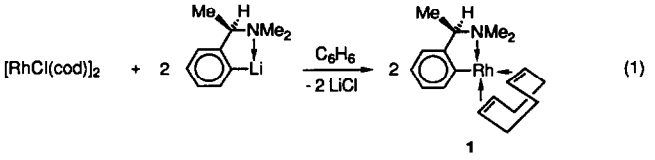
The iridate complexes $Li(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)_2\text{-}Ir(cod)$ (**7**) and $Li(C_6H_4CH_2NMe(^tBu)\text{-}2\text{-}C,N)_2Ir(cod)$ (**8**) were obtained as red powders in quantitative yield in a similar way to that described for the corresponding rhodate complexes.

Mol. weight (cryoscopy in benzene) for $Li(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)_2Ir(cod)$ (**7**); 549 g mol^{-1} (0.13 mol l^{-1}), calcd. for monomeric **7**; 631 g mol^{-1}.

3. Results and discussion

3.1. Synthesis and characterization of $Rh(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)(cod)$ (1)

The transmetallation of $[RhCl(cod)]_2$ with two equivalents of $Li(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)$ (obtained from $(R)\text{-}C_6H_4CH(Me)NH_2$, 96% e.e., see Experimental details) gives a high yield of the orange complex $Rh(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)(cod)$ (**1**), see eqn. (1).



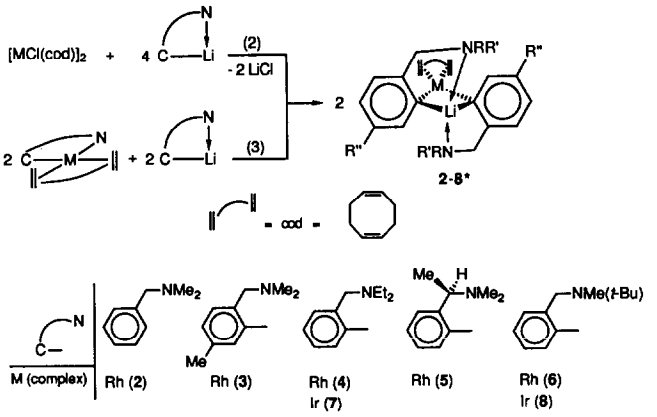
(1)

1

Like many organometallic Rh^I and Ir^I species, complex **1** is air- and moisture-sensitive [7g,h,12]. The ^1H and ^{13}C NMR spectra of complex **1** (see Experimental details) show clearly that it is asymmetric. Since there is a configurationally stable stereogenic centre present in the ligand system then the two resonances observed for the NMe_2 methyl groups in both spectra indicate that Rh–N coordination is inert on the NMR time scale. Further evidence for the Rh–N coordination is provided by a ^{103}Rh coupling constant of 1.5 Hz superimposed on the quartet resonance of the benzylic proton [13]; this coupling is also indicative of rigidity of the chelate ring. The olefinic cod protons afford three complex and fairly broad multiplet resonances, one of which has double intensity, as a consequence of two protons having accidentally coincident chemical shifts. Based on the similarity of the ^1H and ^{13}C NMR spectroscopic features of **1** to those of $Rh(C_6H_3CH_2NMe_2\text{-}2\text{-R-}6\text{-}C,N)(cod)$ (R = H, Me, CH_2NMe_2) containing related achiral ligand systems [12], we suggest that **1** is isostructural with those complexes, *i.e.* it has a square-planar structure, as shown schematically in eqn. (1).

3.2. Synthesis and stability of the -ate complexes 2–8

The rhodate and iridate complexes $Li(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)_2M(cod)$ (M = Rh; $R^1 = CH_2NMe_2$, R^2 = Me (**3**); $R^1 = CH_2NEt_2$, R^2 = H (**4**); R^1 = CH(Me)NMe_2, R^2 = H (**5**); $R^1 = CH_2NMe(^tBu)$, R^2 = H (**6**); M = Ir: $R^1 = CH_2NEt_2$, R^2 = H (**7**); $R^1 = CH_2NMe(^tBu)$, R^2 = H (**8**)) were obtained in high yield from the reaction of $[MCl(cod)]_2$ with 4–5 equivalents of the appropriate arylamine lithium compound in benzene, see eqn. (2) in Scheme 1. The alternative route to the



Scheme 1. Synthetic routes ((2) and (3)) for the -ate complexes **2–8**.

-ate complexes, *i.e.* from a 1:1 reaction of $M(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)(cod)$ and $Li(C_6H_3R^1\text{-}2\text{-}R^2\text{-}5\text{-}C,N)$ is shown in eqn. (3) in Scheme 1.

Surprisingly, the reaction of $[RhCl(cod)]_2$ with an excess of $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$, under the same conditions as described for **3–8** in Experimental details, affords the transmetallation product $Rh(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(cod)$ [12] as the only isolable product; addition of further $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$ does not change the result. However, when the reaction mixture is agitated in an ultrasonic bath the rhodate complex $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2Rh(cod)$ (**2**) is obtained quantitatively. The explanation of this difference is that the poor solubility of $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$ in benzene probably hampers formation of **2** from the initially formed $Rh(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(cod)$. This proposal is supported by the fact that the reaction of $[RhCl(cod)]_2$ and $Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$ carried out in THF, in which the aryllithium compound is soluble, now results in formation of both **2** and $Rh(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(cod)$. The ratio between these two materials depends on the amount of organolithium species added [14*], and it therefore appears that in THF there is an equilibrium between the -ate complex **2** and its precursors, as shown in eqn. (4):

$$Rh(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(cod) + Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N) \quad (4)$$

$$\Vert$$

$$Li(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2Rh(cod)$$

2

Complex **2** can be isolated as a THF-free solid from this reaction mixture, *i.e.* Li–N coordination in **2** is

* Reference number with an asterisk indicates a note in the list of references.

TABLE 1. ^{1}H NMR data for the complexes Li($C_6H_3(R^1)$-2-(R^2)-5-*C,N*)$_2$M(cod) (**2–8**) [a]

R^1	R^2	M	complex	aryl-H	$ArCH_n$–	–NR′R″	HC=CH [b]
CH_2NMe_2	H	Rh	**2**	8.37(d) [c] 7.06(t) [c] 6.95(t) [c] 6.83(d) [c]	4.60(d) [d] 2.75(d) [d]	1.57(s)	4.02 3.91
CH_2NMe_2	Me [e]	Rh	**3**	8.23(s) 6.8(d) [c] 6.75(d) [c]	4.66(d) [d] 2.84(d) [d]	1.63(s)	4.09 4.00
CH_2NEt_2	H	Rh	**4**	8.37(d) [c] 6.9(br m)	4.45(d) [d] 3.48(d) [d]	2.36(m) [f] 2.11(m) [f] 0.34(t) [g]	3.98 3.88
$CH(Me)NMe_2$	H	Rh	**5**	8.42(d) [c] 6.95(br m)	4.91(q) [h]	1.51(s)	4.08 3.84
$CH_2NMe(^tBu)$	H	Rh	**6**	8.34(d) [c] 7.38(d) [c] 7.1(br m)	4.87(d) [d] 4.0(br)	1.74(br s) 1.26(s)	4.30 3.73
CH_2NEt_2	H	Ir	**7**	8.2(d) [c] 7.15(br m)	4.26(d) [d] 3.37(d) [d]	2.35(m) [f] 2.08(m) [f] 0.32(t) [g]	3.56 3.32
$CH_2NMe(^tBu)$	H	Ir	**8**	8.16(d) [c] 7.40(d) [c] 7.23(m) 7.01(t) [c]	4.71(d) [d,i]	1.73(br s) 1.23(s)	3.78 3.18

[a] Recorded in C_6D_6 at room temperature; δ in ppm relative to external TMS; [b] broad second-order multiplets. cod –CH_2– resonances; for **2**, **4**, **6–8** four multiplets at *ca.* 1.7, 2.1, 2.4 and 2.7 ppm; for **3** and **5** two multiplets at 1.9 and 2.4 ppm; [c] ^3J(H,H) = 6–8 Hz; [d] AX pattern, ^2J(H,H) = 10–13 Hz; [e] δ(Ar–CH_3) = 2.28; [f] δ(NCH_2CH$_3$), ^2J(H,H) = 14 Hz, ^3J(H,H) = 7 Hz; [g] δ(NCH$_2$CH_3), ^3J(H,H) = 7 Hz; [h] δ(ArCH(*Me*)) = 1.16(d), ^3J(H,H) = 7 Hz); [i] only one of the two expected resonances is observed at room temperature.

inert towards an excess of THF. This is unexpected, since it is known that lithium normally shows a greater tendency for coordination to oxygen than to nitrogen [15]. For example, addition of THF to solutions of the tetranuclear aggregate [Li($C_6H_4CH_2NMe_2$-2-*C,N*)]$_4$ breaks it down into Li$_2$($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$-(THF)$_4$, in which the N-donor atoms are no longer coordinating [9]. The -ate complexes **2–8** are orange (Rh) or red (Ir) powders, which show extreme sensitivity towards air and moisture * in both the solid state and solution, and decomposition is indicated by a colour change to green (Rh) or blue (Ir) [7g,h,12]. Except for **2**, they are very soluble in benzene, toluene and diethyl ether (at room temperature), and moderately soluble in pentane and hexane. These new complexes have been characterized by ^{1}H, ^{13}C and 2D COSY NMR spectroscopy and molecular weight determination (cryoscopy in benzene, see Experimental details).

It is surprising that in the syntheses of **2–8**, in which an excess of the aryllithium compound is added to [MCl(cod)]$_2$, there is no formation of a high-order -ate complex (Li$_2$(L-*C,N*)$_4$M$_2$), in which the cod ligand has been displaced by two ligands. This contrasts with reactions of alkyl- or aryllithium compounds (LiR) with various cycloocta-1,5-diene and phosphine complexes of platinum and palladium, which do undergo substitution of the coordinated ligands [1b,f]. Our result is however in line with reactions of LiR with cycloocta-1,5-diene or phosphine complexes of iridium and rhodium, which gave -ate complexes containing bridging alkyl or aryl groups, *e.g.* [Li(R)$_2$M(cod)]$_2$ or (tmeda)Li(R)$_2$M(cod) (tmeda = $Me_2NCH_2CH_2$-NMe_2) [1i,j].

In our work the fact that -ate complexes can be obtained with all benzylamine ligand systems used shows that bulk of the N-donor ligand does not influence the stability of the final product. In contrast, the stability of (Et$_2$O)$_x$Li(R)$_2$M(dtbpe) (M = Ir, Rh; R = aryl, alkyl; dtbpe = 1,2-bis(di-^{t}butylphosphino)-ethane) was ascribed to the bulk of the phosphine ligand [1j]. Based on the behaviour of our complexes and of (tmeda)Li(R)$_2$M(cod) [1i], we propose that the important stabilizing effect in these complexes is due not only to the good π-acceptor ability of the cycloocta-1,5-diene ligand (which stabilizes the high electron density on the metal centre) but also to its bidentate character.

The bulky groups on the N-donor atom do indirectly influence the preferred route by changing the solubility of the starting arylamine lithium compounds in benzene, with the order of increasing solubility of the LiL reagents being:

Li($C_6H_4CH_2NMe_2$-2-*C,N*) <
Li($C_6H_4CH_2NEt_2$-2-*C,N*) <
Li($C_6H_4CH_2NMe(^tBu)$2-*C,N*) ≈
Li($C_6H_4CH(Me)NMe_2$-(*R*)-2-*C,N*) ≈
Li($C_6H_3CH_2NMe_2$-2-Me-5-*C,N*).

When the aryllithium compound is slightly soluble in benzene, *e.g.* Li($C_6H_4CH_2NEt_2$-2-*C,N*), a small excess is required to give the best synthetic results since this increases, relatively, the amount of Li reagent in solution. That the solubility is indeed the important factor is proved by the reactions involving Li(C_6H_4-CH_2NMe_2-2-*C,N*) and Li($C_6H_3CH_2NMe_2$-2-Me-5-*C,N*). The former does not dissolve in benzene and -ate complex **2** can only be obtained by use of ultrasonic bath, whereas with the introduction of an Me group on the aryl ring the solubility is now very good, and the -ate complex **3** is readily obtained.

The attempted synthesis of Li(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$Ir(cod), by either route (2) or route (3), showed that the rigid naphthylamine ligand system 1-$C_{10}H_6NMe_2$-8 is not suitable for the formation of an -ate complex [16*]. This result points to the presence of a flexible –CH_2NRR′ moiety as a prerequisite for

* As a consequence recrystallization of these compounds was not successful and micro elemental analysis data obtained on some of the crude isolated materials were variable and unreliable.

TABLE 2. ^{13}C NMR data for the complexes $Li(C_6H_3(R^1)\text{-}2\text{-}(R^2)\text{-}5\text{-}C,N)_2M(cod)$ (3–8) [a]

R^1	R^2	M	complex	aryl				ArCH	NR'R''	cod	
				C(1)	C(2)	C(3–5)	C(6)			=CH	$-CH_2-$
CH_2NMe_2	Me [b]	Rh	3	179.3 [c]	141.6	132.9 [d] 129.2 123.3	146.3	69.9	43.9	86.7(8) 84.5(8)	35.6 28.5
CH_2NEt_2	H	Rh	4	178.9 [e]	145.1	128.9 124.8 122.2	145.6	63.6	41.9 [f,g] 8.2 [f,h]	86.7(8) 85.0(8)	35.7 28.3
$CH(Me)NMe_2$ [i]	H	Rh	5	179.6 [j]	148.8	124.7 124.7 122.1	146.2	66.9	38.8 [f]	86.4(8) 84.6(8)	36.0 28.0
$CH_2NMe(^tBu)$	H	Rh	6	178.3 [k]	149.9 [f]	129.0 [f] 125.9 123.1	139.9 [f]	60.8 [f]	54.9 [l] 34.2 [f,m] 26.9 [f,n]	88.3(8) 82.2(7)	32.2 31.1
CH_2NEt_2	H	Ir	7	175.2 [o]	143.7	130.1 126.4 121.8	144.5	71.1 [f]	42.0 [f,g] 8.2 [f,h]	72.5 62.5	36.6 [f] 28.5 [f]
$CH_2NMe(^tBu)$ [p]	H	Ir	8	n.o.	n.o.	128.5 126.6 122.6	n.o.	59.9	43.1 [m] 26.6 [f,n]	75.1 [f] 68.2 [f]	32.6 31.3

[a] Recorded in C_6D_6 at RT; δ in ppm relative to TMS; $J(^{103}Rh,^{13}C)$ in Hz between parentheses; [b] $\delta(ArCH_3) = 21.5$; [c] $^1J(^{103}Rh,^{13}C) = 37$ Hz, $^1J(^7Li,^{13}C) \sim 9$ Hz; [d] C(5); [e] $^1J(^{103}Rh,^{13}C) = 39$ Hz, $^1J(^7Li,^{13}C) = 8.5$ Hz; [f] broad resonance; [g] $\delta(NCH_2CH_3)$; [h] $\delta(NCH_2CH_3)$; [i] $\delta(ArCH(CH_3)) = 6.6$; [j] $^1J(^{103}Rh,^{13}C) = 39$ Hz, $^1J(^7Li,^{13}C) = 8.7$ Hz; [k] $^1J(^{103}Rh,^{13}C) = 37$ Hz, $^1J(^7Li,^{13}C)$ not resolved; [l] $\delta(NC(CH_3)_3)$; [m] $\delta(NCH_3)$; [n] $\delta(NC(CH_3)_3)$; [o] $^1J(^7Li,^{13}C) \sim 5.5$ Hz; [p] $\delta(NC(CH_3)_3)$ not observed.

obtaining stable -ate complexes. Although the additional Me substituent on the benzylic position in the $-CH(Me)NMe_2$ moiety **4** makes the benzyl ligand system more rigid, it is still clearly flexible enough to afford a stable -ate complex.

3.3. Structural characterization of the -ate complexes 2–8 in solution

3.3.1. General features

The molecular weight determinations (cryoscopy in benzene) ** reveal the -ate complexes to be monomeric, *i.e.* $Li(L\text{-}C,N)_2M(cod)$. The ^1H and ^{13}C NMR spectroscopic data of **2–6** (benzene-d_6) are given in Tables 1 and 2, respectively. Owing to the presence of two additional magnetically active nuclei (^{103}Rh and ^7Li) in these compounds, these NMR data provide detailed information about the solution structures, including geometries and bonding modes of the aryl moieties.

The ^{13}C NMR spectra of **3–6** show both $^1J(^{103}Rh,^{13}C)$ and $^1J(^{13}C,^7Li)$ (see Table 2) on the C_{ipso} resonances of the ligand systems, indicating the aryl group bridges between rhodium and lithium. As a representative example the C_{ipso} resonance of **4** is shown in Fig. 1.

Furthermore, ^1H and ^{13}C NMR spectroscopies show the presence of one rhodium-coordinated cod ligand. In the ^{13}C NMR spectra of **3–6** the two resonances of the olefinic carbon of cod are not so widely separated as those in the precursor M(L-*C,N*)(cod) complexes (2–10 ppm *versus* 14–20 ppm, respectively) [7a,b,12]. For **3** and **4** the $J(^{103}Rh,^{13}C)$ value for both of these resonances is *ca.* 8 Hz. In Rh(L-*C,N*)(cod), with two different ligands (C and N) *trans* to the olefinic moieties, these coupling constants are 8 and 15 Hz [7a,b,12]. We therefore suggest that in the -ate complexes **3–6** the same ligand is present *trans* to both olefinic moieties, *i.e.* the C atom of the aryl ligand. From the ^1H NMR spectra the principal coordination mode of the amine function is clear from the highfield shift of the nitrogen substituents compared to those in the non-metallated arylamine ligand precursor. In the aromatic region of the these complexes, the doublet at *ca.* 8.3 ppm is assigned to the *ortho* proton. Relative to that for the square-planar M(L-*C,N*)(cod) complexes (*ca.* 7.1 ppm) [7a,b,g,h,12], this doublet resonance is at significantly lower field ($\Delta\delta = 1.2$ ppm), but at almost the same position as that for the *ortho* proton in analogous Li compounds [7h], *i.e.* this is an extra indirect indication of the presence of lithium. On the basis of the combined data, we suggest that the -ate

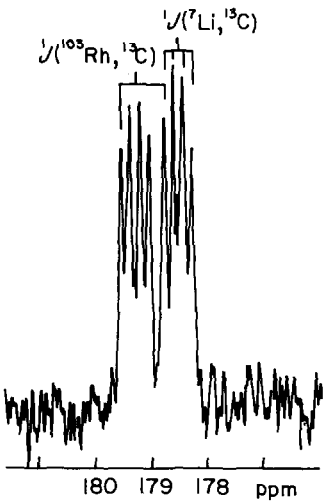


Fig. 1. The resonance for C_{ipso} in **4**, showing coupling to both ^{103}Rh and ^7Li.

* Reference number with asterisk indicates a note in the list of references.

** As representative examples molecular weight determinations by cryoscopy have been carried out for **4** and **7**. Due to the limited solubility of **2**, **3**, **5**, **6** and **8** near the melting point of benzene (partial crystallization of the compounds occurred) no reliable data could be obtained.

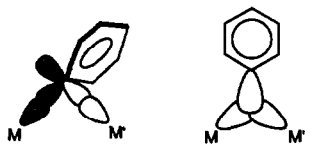


Fig. 2. The two types for the three-centre two-electron bonding mode, *i.e.* asymmetric (a) with $M \neq M'$ *versus* symmetric (b) with $M = M'$.

complexes are heterodinuclear, as depicted in Scheme 1, with the rhodium centre in a square-planar coordination geometry formed by two mutually *cis* olefinic moieties and two aryl ligands, which both further bridge, through the C_{ipso} atoms, to a Li atom whose tetrahedral coordination geometry is completed by intramolecular coordination of two amine groups. Comparison of specific NMR data allows us to characterize the bridging mode of the aryl groups quite accurately. The ^{103}Rh coupling constants for the C_{ipso} resonances of **3–6** are similar to those found for other Rh complexes containing a direct Rh–aryl σ-bond (*e.g.* **1**) [7h,12], and indicate the presence of such a bond in these -ate complexes. The ^{13}C–^{7}Li coupling constant is substantially smaller than those for other aryllithium compounds [17,18]; for aryl ligands bridging two Li centres in a three-centre two-electron bonding mode, the value of $^{1}J(^{13}C,^{7}Li)$ is *ca.* 20 Hz, and it is *ca.* 12 Hz when the aryl group is bonded to three Li centres in a four-centre two-electron bonding mode [17,18]. However, when C_{ipso} is bridging unlike metal centres (as in organocuprates or -argentates of the type $L_4M_2Li_2$ having similar C,N ligand systems) then a smaller $^{1}J(^{13}C,^{7}Li)$ is also found [11,10]. Therefore, the -ate complexes **3–6** probably contain an asymmetric type of bridge as shown in Fig. 2a rather than the symmetric type of CLi_2 bridge (Fig. 2b), as found in dimeric aryllithium species $Li_2L_2(Et_2O)_4$. In the proposed dinuclear structure of **3–6** each of the two bridging aryl groups is colinear with respect to its $M–C_{ipso}$ σ-bond and, consequently, perpendicular to the corresponding $Li–C_{ipso}$ bond. The latter is, more or less, a π-type bond with a low s-character that provides a small $J(^{13}C,^{7}Li)$ value [11].

Because of the great similarity of the chemical shifts in both the ^{1}H and ^{13}C NMR spectra (see Tables 1 and 2, respectively) of the iridate complexes **7** and **8**, these compounds can be expected to be isostructural with the corresponding rhodate complexes **4** and **6**, respectively. It should be noted, however, that the observed $^{1}J(^{13}C,^{7}Li)$ value in **7** (~ 5.5 Hz) is significantly smaller than that in the corresponding rhodate complex **4** (8.5 Hz).

3.3.2. Fluxional behaviour of 2–4

As a consequence of the bridging bonding mode of the aryl group between two different metals the two bridging C_{ipso} atoms are chiral centres. The proposed

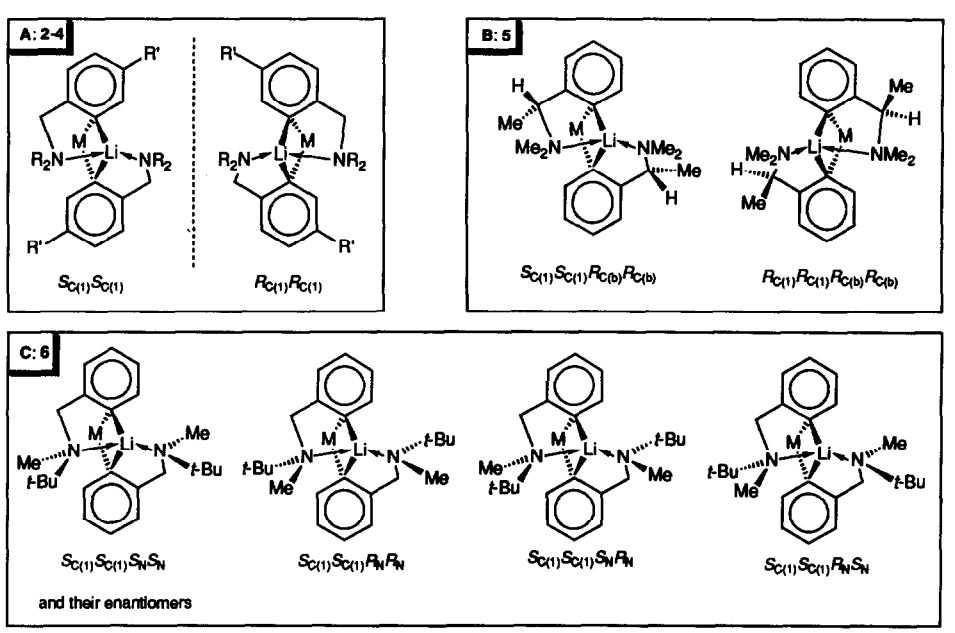


Fig. 3. The possible diastereoisomers for the rhodate complexes with the cod ligand omitted for clarity. Figure A applies to $Li(C_6H_3CH_2NR_2\text{-}2\text{-}R'\text{-}5\text{-}C,N)_2Rh(cod)$ (R = Me, R' = H (**2**); R = R' = Me (**3**); R = Et, R' = H (**4**), B applies to $Li(C_6H_4CH(Me)NMe_2\text{-}(R)\text{-}2\text{-}C,N)_2Rh(cod)$ (**5**) and C applies to $Li(C_6H_4CH_2NMe(^tBu)\text{-}2\text{-}C,N)_2Rh(cod)$ (**6**). C(1) is the *ipso* carbon atom and C(b) the benzylic carbon atom.

structure (see Scheme 1) requires that both chiral centres have the same configuration, as was unambiguously shown for the chiral rhodate complex Li(C_6H_4-CH(Me)NMe_2-(*R*)-2-*C*,*N*)$_2$Rh(cod) (**5**) (*vide infra*). The complexes **2–4** show fluxional behaviour associated with the Li–N coordination (*vide infra*). In the limiting situation, *i.e.* inert coordination of the N-donor atoms, there is always one nitrogen function coordinating above and one coordinating beneath the $(C_{ipso})_2$RhLi plane. Thus for **2–4** the two enantiomers that may be formed ($S_{C(1)}S_{C(1)}$ and $R_{C(1)}R_{C(1)}$; C(1) = C_{ipso}), see Fig. 3A, are indistinguishable by NMR spectroscopy.

In the solution ^{1}H NMR spectra of **2–4** at room temperature the chirality of the C_{ipso} atoms is reflected in the observation of an AX pattern for the benzylic $-CH_2-$ resonances. Owing to its good solubility and simple resonance patterns, results for complex **3** are discussed as representative of the variable temperature NMR experiments on these complexes with $[C_6H_4CH_2NR_2$-2$]^-$ ligand systems. Since no coalescence of the AX pattern of **3** is observed up to 381 K (at this temperature, the highest employed, decomposition of **3** into Rh($C_6H_3CH_2NMe_2$-2-Me-5-*C*,*N*)(cod) and $C_6H_4CH_2NMe_2$-Me-4 becomes observable) it can be inferred that a process involving continuous inversion of configuration of the bridging C_{ipso} atom (*i.e.* "rotation" of the aryl group around the C_{ipso}–C_{para} vector) is slow on the NMR time scale or does not occur at all.

However, a fluxional process does operate, involving Li–N dissociation/association and pyramidal inversion at nitrogen, because the protons of the nitrogen substituents in the ligand systems are enantiotopic (the Me groups give one broad resonance) over the whole high temperature range of 300 to 380 K. If the Li–N coordination were inert on the NMR timescale, then the prochiral $-NMe_2$ group would be stereogenic and give rise to two singlet resonances. When the temperature is lowered the $-NMe_2$ protons do afford two singlets at 213 K (coalescence temperature *ca.* 230 K); the two Me groups are now diastereotopic as a consequence of inert Li–N coordination. An interesting observation is that the highfield doublet of the AX pattern is much broader at 253 K than at higher temperatures, whereas the low-field doublet remains sharp from 210 to 380 K. Two possible explanations for this behaviour are presented below.

3.3.3. Fluxional behaviour of 5; stereochemical assignment

In addition to the two bridging chiral C_{ipso} centres in **2–4**, in **5** the two benzylic carbon atoms are also chiral. Since **5** was prepared starting from enantiomerically pure Li(C_6H_4CH(Me)NMe_2-(*R*)-2-*C*,*N*) it is obvious that in **5** these chiral benzylic carbon atoms both have the same *R* configuration. As has been outlined for **2–4** (*vide supra*) both of the two bridging C_{ipso} atoms have either an *R* or an *S* configuration. For **5** this results in two possible diastereoisomeric structures, *i.e.* $S_{C(1)}S_{C(1)}R_{C(b)}R_{C(b)}$ and $R_{C(1)}R_{C(1)}R_{C(b)}R_{C(b)}$, as schematically shown in Fig. 3B. Since the ^{1}H and ^{13}C NMR spectra of **5** show only one resonance pattern for the arylamine ligand system over the whole temperature range studied (213 K to 300 K), alternative structures in which the two bridging C_{ipso} atoms have different configurations may be excluded. If these atoms had different configurations there would be two diastereoisomeric ligand systems (*i.e.* $S_{C(1)}R_{C(b)}$ and $R_{C(1)}R_{C(b)}$) present within each molecule of complex **5**, and this would give rise to two resonance patterns in the limiting situation.

Another important conclusion that can be drawn from the fact that complex **5** affords only one arylamine resonance pattern is that it is stereoselectively formed as one diastereoisomer. On the basis of the ^{1}H and ^{13}C NMR spectroscopic data it is impossible to distinguish between the two possible diastereoisomeric structures ($S_{C(1)}S_{C(1)}R_{C(b)}R_{C(b)}$ or $R_{C(1)}R_{C(1)}R_{C(b)}R_{C(b)}$) of Fig. 3B. However, from further consideration of the steric hindrance by using molecular models we can distinguish between these two diastereoisomers and thereby assign the configuration at C_{ipso}. In the $S_{C(1)}S_{C(1)}R_{C(b)}R_{C(b)}$ diastereoisomer the benzylic Me substituents point inwards over the $(C_{ipso})_2$RhLi plane. This results in more steric hindrance than in the $R_{C(1)}R_{C(1)}R_{C(b)}R_{C(b)}$ diastereoisomer, in which the Me substituents now point outwards, and so we suggest that **5** is the $R_{C(1)}R_{C(1)}R_{C(b)}R_{C(b)}$ diastereoisomer.

As for **2–4**, the ^{1}H and ^{13}C NMR spectra of **5** at room temperature show that there is fluxionality; *i.e.* the Me groups of the $-NMe_2$ moiety that were diastereotopic at 213 K are now enantiotopic (one broad resonance), and thus Li–N dissociation/association with pyramidal inversion at nitrogen, is occurring. However, it is not possible to exclude the presence of an equilibrium between the two diastereoisomers at room temperature (brought about by a fluxional process in which there is rotation of the aryl group around the C_{ipso}–C_{para} vector), because **5** lacks the prochiral benzylic probe.

3.3.4. Fluxional behaviour of 6

Compared to that for **2–5** a much more complicated NMR situation arises for the rhodate complex **6**, which has a more complex stereochemistry than **5**. Owing to the presence of the different substituents (Me and ^{t}Bu) on the N-donor atoms, these two nitrogen atoms are both potential centres of chirality, but they only have

stable configurations (R_N or S_N) when Li–N coordination is inert on the NMR time scale. Because both pyramidal inversion at N and C–N bond rotation are low-energy processes [19], we can expect a variety of diastereoisomers of **6** to be present in solution, namely $S_{C(1)}S_{C(1)}S_NS_N$, $S_{C(1)}S_{C(1)}R_NR_N$, $S_{C(1)}S_{C(1)}S_NR_N$ and $S_{C(1)}S_{C(1)}R_NS_N$ or their enantiomeric forms, see Fig. 3C.

Whereas the ^{1}H NMR spectrum at room temperature of the other -ate complexes show the benzylic $-CH_2-$ protons as a sharp AX or AB pattern, the ^{1}H NMR spectrum of rhodate complex **6** shows one sharp doublet at low field and one broad resonance at high field (as found for **3** at low temperature). Homonuclear decoupling NMR experiments on **6** at room temperature in which the lowfield resonance was irradiated did not result in significant change in the shape of the broad resonance at higher field. Nevertheless, 2D ^{13}C, ^{1}H COSY (Correlation Spectroscopy) and APT (Attached Proton Test) NMR experiments with the analogous iridate complex **8** at room temperature do confirm the assignment of the broader resonance as the second benzylic proton. For **6**, the latter benzylic resonance at *ca.* 4 ppm sharpens to a doublet form when the temperature is raised to 323 K, and decoupling of the lowfield doublet at this temperature does result in a singlet resonance. The resonances of the –NMe and –N(^{t}Bu) protons and the aromatic *ortho* proton are also sharper at this temperature than at room temperature, indicating that the association/dissociation including pyramidal inversion of the N atom process is now faster on the NMR time scale. The ^{1}H NMR spectrum of a toluene-d_8 solution of **6** at 213 K shows an additional new AB pattern at 5.5 and 5.1 ppm with a $^2J(^1H,^1H)$ value of 15 Hz; the AX pattern found at room temperature is still present, with the same shape as at room temperature, *i.e.* one sharp and one broad resonance. In the same spectrum the olefinic cod protons give rise to three multiplets, one with double intensity, and in the aromatic region there are two doublets at *ca.* 8.8 and 8.2 ppm and a broad resonance at *ca.* 7.9 ppm. The $NC(CH_3)_3$ protons now appear as a broad resonance at 1.5 ppm and for the NCH_3 protons there are two broad resonances at 0.7 and 2.5 ppm; the $NC(CH_3)_3$ and NCH_3 protons have different coalescence temperatures. These data indicate that the fluxional process observed at high temperature is now frozen out and, as shown by the integrals, two diastereoisomers are present in a 1:1 ratio. The diastereotopicity can arise either from different rhodate molecules (the two structures on the left in Fig. 3C) or from the ligand systems within one rhodate molecule (one of the two structures on the right in Fig. 3C). Which of these two situations applies to **6** can be examined by ^{13}C NMR spectroscopy at low temperature, and the resonances of the C_{ipso} atom provide the simplest information. Considering the four diastereoisomeric possibilities given in Fig. 3C, the following situations can be distinguished. The $S_{C(1)}S_{C(1)}S_NS_N$ and $S_{C(1)}S_{C(1)}R_NR_N$ diastereoisomers each contain two identical ligand configurations and thus each give one resonance for the C_{ipso} atom, whereas the $S_{C(1)}S_{C(1)}S_NR_N$ and $S_{C(1)}S_{C(1)}R_NS_N$ diastereoisomers, with two non-identical ligand configurations, each give the same two resonances for the C_{ipso} atom (for the enantiomeric forms with the *R*-configuration on C_{ipso} one obtains identical resonances). The ^{13}C NMR spectrum of **6** at 213 K shows two doublet resonances for the C_{ipso} atoms, at 177.2 and 180.3 ppm, both with a $J(^{103}Rh,^{13}C)$ value of 37.7 Hz, and four olefinic resonances between 80 and 90 ppm, and the rest of the spectrum is also doubled. This indicates that at 213 K, either a mixture of the $S_{C(1)}S_{C(1)}S_NS_N$ and $S_{C(1)}S_{C(1)}R_NR_N$ diastereoisomers or one of the $S_{C(1)}S_{C(1)}S_NR_N$ or $S_{C(1)}S_{C(1)}R_NS_N$ diastereoisomers is present; every other combination can, on the basis of the anticipated C_{ipso} resonances, be ruled out. Molecular models show that steric hindrance between the two neighbouring ^{t}Bu groups in the $S_{C(1)}S_{C(1)}S_NS_N$ diastereoisomer and, consequently, the $S_{C(1)}S_{C(1)}R_NR_N$ diastereoisomer, precludes these forms. Thus, the enantiomers $R_{C(1)}R_{C(1)}R_NR_N$ and $R_{C(1)}R_{C(1)}S_NS_N$ can also be ruled out. Therefore, at 213 K the rhodate complex **6** exists as one molecule containing two diastereoisomeric ligand systems having the configuration $S_{C(1)}S_{C(1)}S_NR_N$ or $S_{C(1)}S_{C(1)}R_NS_N$ ($R_{C(1)}R_{C(1)}R_NS_N$ or $R_{C(1)}R_{C(1)}S_NR_N$, respectively).

3.4. A comparison of 2–8 with other -ate complexes

Structural characterization of **2–8** shows clearly that they are iridate and rhodate complexes involving intramolecular coordination of an amine ligand (ICAL). Several other examples of metallate complexes (M = Cu, Ag) *with* ICAL [11], or iridate and rhodate complexes *without* ICAL are known [1i,j], but **2–8** are the first examples of metallate complexes of the cobalt triad in combination with ICAL. An important feature of ICAL is that it hinders dimerization of the -ate complexes; dimerization was observed for cycloocta-1,5-diene-containing -ate complexes without Lewis bases [1i].

From a structural comparison of **2–8** with the complex $Cu_4(C_6H_4CH(Me)NMe_2\text{-}(S)\text{-}2\text{-}C,N)_4$ [1d], we conclude that the new $Li(L)_2M(cod)$ complexes also contain puckered five-membered chelate rings, as shown in the right-hand schematic representation of **2–8** in Fig. 4.

A consequence of this puckering is that the benzylic

2-8

Fig. 4. The schematic representation of the -ate complexes showing the puckering of the five-membered chelate rings.

$-CH_2-$ protons in the ^1H NMR spectrum of the -ate complexes give one sharp and one broad doublet resonance under certain conditions under which the fluxionality of the $-CH_2NRR'$ moiety is expected to be slow on the NMR time scale. One explanation is that the broadening may be due to a significant (though unresolved) small $^{103}Rh-^1H$ coupling arising from a favourable dihedral angle between this proton and the metal centre. However, we think that the broadening is more likely to be the result of direct interaction of the transition metal centre with the benzylic proton that is much closer to the C_2MLi plane than the other.

From the variable temperature NMR data for the -ate complexes **3–6** it is possible to make a reasonable deduction concerning the mechanism of the fluxionality observed. Fluxionality in the -ate complexes (tmeda)Li$(R)_2$M(dtbpe) has been previously attributed to a 'rocking' motion of the Li(tmeda) unit about the $C_{ipso}-C_{ipso}$ vector by which the lithium centre is forced towards the transition metal centre [1j]. For our complexes **2–8** such a 'rocking' motion need not be considered because it is fully blocked by the intramolecular coordination of the chelating amine ligand. Therefore, the likely combined processes occurring in our complexes are dissociation/association of the N-donor atom from Li, pyramidal inversion at this nitrogen atom, and rotation around the $N-C_{benzyl}$ axis. At 323 K this fluxionality is fast on the NMR time scale for all -ate complexes studied. However, as the temperature is lowered, even at 295 K, complexes **6** and **8**, with the sterically demanding $CH_2NMe(^tBu)$ moiety, are at the slow exchange limit, whereas complex **3** with the smaller $-CH_2NMe_2$ moiety reaches this limit only at 243 K. Although the $NMe(^tBu)$ group is more weakly coordinating than the NMe_2 group [7d], in the process where rotation around the $N-C_{benzyl}$ axis occurs the bulky ^tBu substituent provides more steric hindrance than an Me group and so confers on complexes **6** and **8** the highest kinetic stability among the -ate complexes we have investigated.

Since all the -ate complexes **3**, **4**, **6–8** show two sharp doublet resonances for the benzylic protons at temperatures between 323 and 381 K (where fluxionality is fast on the NMR time scale) we conclude that in the fluxional process rotation of the aryl ring about the $C_{ipso}-C_{para}$ axis is not operative. In contrast, it has been reported that this type of rotation process does operate in the complex $Li_2(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_4M_2$ (M = Cu, Ag or Au); *i.e.* the iridate and rhodate complexes are more stable with respect to inversion of configuration at C_{ipso}.

4. Conclusions

The synthesis and characterization by NMR spectroscopy of a new series of rhodate and iridate complexes Li$(L)_2$M(cod) containing two chelating arylamine ligand systems is described. From the ^{13}C NMR data it is clear that the C_{ipso} atom is bonded to both the lithium centre and either a rhodium or an iridium centre, and on the basis of combined ^1H and ^{13}C NMR data the new complexes are suggested to be heterobimetallic -ate complexes. The late transition metal centre is in a square-planar environment and the lithium atom has a tetrahedral geometry. The overall structure of these heterodinuclear species is associated with an equivalent chiral configuration of the two C_{ipso} atoms. This feature results in diastereoselective product formation for ligands containing the CH_2NR_2 or the $CH_2NMe(^tBu)$ moiety, whereas for ligands containing the $CH(Me)NMe_2$ moiety there is both diastereoselective and enantioselective product formation. Intramolecular coordination of N-donor atoms to lithium in these species prevents dimerization, *i.e.* the *ortho*-amine moiety can be considered to function as an intramolecularly-positioned solvent molecule.

Contrary to first expectations, the use of sterically more bulky substituents at the N-donor site of the arylamine ligand makes the resulting -ate complexes more readily accessible and more stable with respect to fluxionality.

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