Ligand Substitution Reactions in New Square-planar Iridium, Rhodium and Platinum Complexes containing a Potentially Terdentate C,N,N′ Ligand System; Crystal Structure of [Ir{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N,N′*}(cod)] (cod = cycloocta-1,5-diene)†

Ingrid C. M. Wehman-Ooyevaar,[a] **G. Marc Kapteijn,**[a] **David M. Grove,**[a] **Wilberth J. J. Smeets,**[b] **Anthony L. Spek**[b] **and Gerard van Koten** *[,a]
[a] *Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b] *Bijvoet Center for Biomolecular Research, Vakgroep Kristal-en Structuurchemie, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Transmetallation reactions with the new dimeric compound $[LiL]_2$ [L = $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2] have incorporated the potentially terdentate monoanionic C,N,N′ ligand system L into the new complexes [M^{I}L(cod)] (M = Rh or Ir, cod = cycloocta-1,5-diene) and [Pt^{II}Cl(L)] which have been characterized by ^1H and ^{13}C NMR spectroscopy. In solution these complexes are square-planar with L co-ordinated as a C,N bidentate in [ML(cod)] and as a C,N,N′ terdentate in [PtCl(L)]. However, the solid-state molecular structure of [IrL(cod)] shows a C,N,N′ terdentate co-ordination mode of L; the square-pyramidal geometry reflects a situation in the direction of the reaction transition state of a nucleophile (NMe_2) attacking a d^8 metal centre. Crystals of [IrL(cod)]($C_{20}H_{31}IrN_2$) are orthorhombic, space group $P2_12_12_1$, with *a* = 7.956(3), *b* = 14.090(1), *c* = 16.484(2) Å, *Z* = 4, final *R* = 0.0284 for 2078 reflections with $I \geqslant 2.5\sigma(I)$ and 221 parameters. The neutral monodentate ligands CO and PPh_3 replace the bidentate cod ligand in [ML(cod)] (M = Rh or Ir) to afford complexes which in solution on the NMR time-scale are fluxional and in which L is either bi- or ter-dentate.

Terdentate chelating ligands have proven to be very useful in organometallic chemistry,[1] and they have several specific capabilities that include not only stabilization of a variety of metal oxidation states but also control of both reaction and complex stereochemistry as a result of the geometric restrictions they impose. There are now important terdentate ligand systems known based on P-donor atoms,[1d,h,m,o–q] N-donor atoms,[1a,e,i,k,l,n] and a combination of P- and N-donor atoms.[1g,j] Regarding the nitrogen-based ligands, although some of their complexes possess six-membered chelate rings,[1a,e,i,n,2] more commonly the N-donor atoms are found in five-membered chelate rings.[1k,l,2] We have extensively studied the monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (*trans*-pincer) which is a potentially terdentate N,C,N′-chelating system. In most complexes of the late-transition metals with this ligand one finds N,C,N′ co-ordination and two five-membered M–C–C–C–N chelate rings with a common M–C bond. Because of geometric constraints the two *N*-donor ligands are never exactly *trans* to each other but, generally, the metal and the ligating N,C,N′ atoms are in one plane; in square-planar and octahedral species the ligand co-ordination can be described as meridional and in trigonal-bipyramidal species approximate axial–equatorial–axial spanning is known.[1b,c,f,l,3] When necessary this ligand can accommodate other geometries such as square pyramidal and recently in the tantalum alkylidene complex [$TaCl_2${$C_6H_3(CH_2NMe_2)_2$-2,6-*N,C,N′*}($CHBu^t$)] the N-donor atoms were found, unusually, to be close to mutually *cis* and the N,C,N′ bonding mode was then pseudo-facial with N–Ta–N of 118.63(14)°.[4] The ligand can also function as a C,N bidentate system as in the rhodium(I) and iridium(I) complexes [M{$C_6H_3(CH_2NMe_2)_2$-2,6-*C,N*}(cod)] (cod = cycloocta-1,5-diene), where one N-donor atom does not co-ordinate due to steric hindrance from the bidentate co-ordinated cod.[5] For the iridium complex this steric hindrance results in a very interesting intramolecular isomerization of the ligand to afford [Ir{$C_6H_3(CH_2NMe_2)_2$-2,4-*C,N*}(cod)].[6] Reactions of the rhodium complex with π-acceptor molecules afforded complexes with only *C*-co-ordination of the ligand and non-co-ordination of both N-donor atoms, *e.g.* [Rh{$C_6H_3(CH_2NMe_2)_2$-2,6-*C*}(cod)(CO)].[5b]

In an extension of our studies into bonding modes and influences of aryl ligands having substituents with N-donor atoms in organometallic complexes of the late-transition metals, we now describe the synthesis of new rhodium, iridium and platinum complexes based on our recently developed aryl ligand system $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]^-$ (*cis*-pincer).‡ This system is also a potentially terdentate ligand, but differs from the *trans*-pincer ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ in two ways. First, when co-ordinated as a terdentate, it should always give *cis*-co-ordinated nitrogen atoms. Secondly, when the $-CH_2CH_2NMe_2$ unit is not co-ordinating, its flexibility can still enable the N-donor atom closely to approach the metal centre. In this situation this unit, a Lewis base may become an active spectator moiety and provide anchimeric assistance in metal-centred reactions. Therefore, reactions of the new complexes have been carried out with several reagents, but in particular CO because of its role in catalytic reactions such as the functionalization of C–H bonds.[8]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ Two approaches to this system are available, namely orthometallation of $C_6H_5CH_2N(Me)CH_2CH_2NMe_2$,[7a] and ortholithiation of $C_6H_4BrCH_2N(Me)CH_2CH_2NMe_2$-2.[7b]

Experimental

General.—Syntheses were carried out using standard Schlenk techniques in an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. The compounds $[LiC_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]_2$ **1**,[7b] $[\{IrCl(cod)\}_2]$[9] (an improved version of that given in ref. 10), $[\{RhCl(cod)\}_2]$[11] and *cis*-$[PtCl_2(SEt_2)_2]$[12] were prepared by literature methods. ^1H, ^{13}C and ^{31}P and two-dimensional NMR spectra were recorded on Bruker AC 200 and AC 300 spectrometers. Standard pulse sequences were used for correlation spectroscopy (COSY) experiments and the time data [200 MHz; typically 512 × 1024 points in t_1 and t_2, respectively, acquired with 32 scans (2 dummy) per increment] were processed with a shifted sine-bell window function.[13] Infrared spectra were recorded on a Perkin Elmer 283 spectrophotometer. Elemental analyses were obtained from the section Elemental Analyses of the Institute for Applied Chemistry TNO, Zeist, The Netherlands and from Dornis und Kolbe, Mikroanalytisches Laboratorium, Mühlheim a.d. Ruhr, Germany.

Synthesis of $[Ir\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(cod)]$ **2**.—A solution of **1** (0.82 g, 2.05 mmol) in C_6H_6 (15 cm^3) was added slowly to a solution of $[\{IrCl(cod)\}_2]$ (1.36 g, 2.03 mmol) in C_6H_6 (20 cm^3). After the red suspension had been stirred for 30 min, it was centrifuged and the supernatant solution collected by decantation under N_2. The solid (LiCl) was then washed with C_6H_6 (2 × 10 cm^3). The combined C_6H_6 supernatant and washings were concentrated *in vacuo* to afford a red oil. This was triturated with pentane (5 × 10 cm^3) to afford **2** as an orange powder (1.86 g, 93%) (Found: C, 48.05; H, 6.15; N, 5.55. $C_{20}H_{31}IrN_2$ requires C, 48.85; H, 6.35; N, 5.70%). Crystals of **2**, suitable for a single-crystal X-ray diffraction study, were grown by leading a slow N_2 stream over a saturated pentane solution of **2** at room temperature.

Synthesis of $[Rh\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(cod)]$ **3**.—To a solution of $[\{RhCl(cod)\}_2]$ (1.0 g, 2.03 mmol) in C_6H_6 (20 cm^3) was added slowly a solution of **1** (0.82 g, 2.05 mmol) in C_6H_6 (15 cm^3). Subsequent work-up as described for **2** afforded **3** as an orange powder (1.58 g, 97%) (Found: C, 58.50; H, 7.60; N, 6.75. $C_{20}H_{31}N_2Rh$ requires C, 59.70; H, 7.75; N, 6.95%).

Synthesis of $[PtCl\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}]$ **4**.—A solution of **1** (2.25 g, 5.65 mmol) in C_6H_6 (15 cm^3) was added dropwise to a solution of *cis*-$[PtCl_2(SEt_2)_2]$ (5.0 g, 11.2 mmol) in C_6H_6 (25 cm^3). After stirring for 2 h the resulting off-white suspension was evaporated *in vacuo* to dryness. The yellow residue was extracted with CH_2Cl_2 (2 × 25 cm^3) and the combined yellow CH_2Cl_2 extracts were evaporated *in vacuo* to afford a pale yellow oil. Upon addition of Et_2O (15 cm^3), a white solid precipitated. This was collected by filtration, washed with Et_2O (15 cm^3) and dried in air affording **4** as a white powder (3.81 g, 81%). ^1H NMR (CD_2Cl_2, room temperature) δ 7.27 [d, 1 H, H of aryl, $^3J(^{195}PtH)$ 44, $^3J(HH)$ 6–8], 6.78–7.03 (m, 3 H), 4.30, 3.82 [AB, 2 H, $C_6H_4CH_2N$, $^3J(^{195}PtH)$ 106, $^2J(HH)$ 13–15], 2.91 [s, 3 H, NMe, $^3J(^{195}PtH)$ 49], 2.78, 2.82 (2 × s, 6 H, NMe_2, ^{195}Pt satellites observed as shoulders), 3.57 [td, 1 H, $(CH_2)_2$, $^2J(HH)$ 13, $^3J(HH)$ 3], 3.23 [td, 1 H, $(CH_2)_2$, $^2J(HH)$ 13, $^3J(HH)$ 3 Hz] and 2.8 [m, 2 H, $(CH_2)_2$] (Found: C, 34.20; H, 4.55; N, 6.60. $C_{12}H_{19}ClN_2Pt$ requires C, 34.15; H, 4.55; N, 6.65%).

Ligand Substitution Reactions of Complexes **2** *and* **3**.—(*a*) *Reaction of complex* **2** *with* CO; *in* situ *formation of* $[Ir\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(cod)(CO)]$ **5** *and* $[Ir\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(CO)_2]$ **6**. Through a solution of **2** (0.1 g, 0.2 mmol) in dry $[^2H_8]$toluene (1 cm^3) was bubbled CO at −60 °C. After 30 s, 0.5 cm^3 of this yellow solution was transferred to a pre-cooled 5 mm o.d. NMR tube and the ^1H NMR spectrum, measured at −60 °C, showed quantitative formation of **5**. At this temperature, **5** was stable towards extra CO addition. When CO was bubbled through this $[^2H_8]$toluene solution of **5** at room temperature for *ca.* 7 min (total time), the ^1H NMR spectrum then showed that **6** was formed quantitatively. Complex **6**: $\tilde{\nu}_{max}/cm^{-1}$ (CO) 1964 and 2038 (C_6D_6).

(*b*) *Reaction of complex* **3** *with* CO; *in* situ *formation of* $[Rh\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(CO)_2]$ **7** *and* $[Rh\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}(CO)]$ **8**. Through a solution of complex **3** (0.1 g, 0.25 mmol) in C_6D_6 (2 cm^3) was bubbled CO at room temperature. After 30 s, 0.5 cm^3 of the resulting yellow solution was transferred to a 5 mm o.d. NMR tube; the ^1H NMR spectrum showed that the dicarbonyl complex **7** was formed quantitatively. Evaporation of the remaining reaction solution *in vacuo* afforded an orange powder whose ^1H NMR spectrum (C_6D_6) showed it to be the monocarbonyl complex **8**. When CO was bubbled through this solution, complex **7** was reformed: $\tilde{\nu}_{max}/cm^{-1}$ (CO) 1933, 1985, 2015 and 2040 (C_6D_6).

Synthesis of $[Rh\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}(CO)]$ **8**.*—Through a solution of complex **3** (0.25 g, 0.62 mmol) in C_6H_6 (10 cm^3) was bubbled CO for 2 min. After 10 min of additional stirring in a CO atmosphere, the yellow solution was evaporated *in vacuo* to dryness. This solid was washed with pentane (2 × 5 cm^3) and dried *in vacuo* to afford **8** as a yellow-orange powder (0.19 g, 95%); $\tilde{\nu}_{max}/cm^{-1}$ (CO) 1915 (KBr), 1932 (C_6D_6).

Synthesis of $[Rh\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}(PPh_3)]$ **9**.*—Solid PPh_3 (0.2 g, 0.76 mmol) was added to a solution of complex **3** (0.3 g, 0.75 mmol) in C_6H_6 (10 cm^3). After 5 min of stirring the solution was evaporated *in vacuo* to an oily residue. This was washed with pentane (2 × 5 cm^3) and dried *in vacuo* to afford **9** as a yellow powder (0.38 g, 90%). $\delta_P(C_6D_6)$ 66.3 [d, $^1J(RhP)$ 244 Hz].

X-Ray Data Collection, Structure Determination and Refinement of Complex **2**.—A yellow rod-shaped crystal was introduced into a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4 diffractometer for data collection. Unit-cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $12.8 < \theta < 17.5°$. Unit-cell parameters were checked for the presence of higher lattice symmetry.[14] Data for one octant were collected twice, averaged, corrected for Lorentz-polarization, for absorption (DIFABS;[15] correction range 0.914–1.187) and for a linear decay of 4.1% as observed in the intensity control reflections during the 76 h of X-ray exposure time. The structure was solved with standard Patterson methods (SHELXS 86)[16] and a series of subsequent Fourier difference analyses. Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, H atoms with one common isotropic parameter [$U = 0.096(8)$ Å^2]. Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.0284$, $R' = 0.0308$ $\{w = 1/[\sigma^2(F) + 0.000\,32F^2]\}$. The absolute structure was checked by refinement with opposite anomalous dispersion factors $(-if'')$ resulting in $R = 0.0291$ and $R' = 0.0331$. Crystal data and numerical details of the structure determination are listed

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* This rhodium(I) complex, obtained by precipitation as a crude product, has been characterized spectroscopically but has not afforded satisfactory elemental analysis data. Our failure to purify this complex is to some extent related to its air-sensitivity but has primarily its origin in donor-ligand dissociation processes and some lithium salt contamination resulting from the minimum purity of the extremely air-sensitive precursor complex **3**.

Table 1 Crystal data and details of the structure determination for complex **2**

(*a*) Crystal data	
Formula	$C_{20}H_{31}IrN_2$
M	491.70
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a/Å	7.956(3)
b/Å	14.090(1)
c/Å	16.484(2)
U/Å^3	1847.8(7)
Z	4
D_c/g cm^{-3}	1.767
F(000)	968
μ(Mo-Kα)/cm^{-1}	72.0
Crystal size/mm	1.00 × 0.20 × 0.20

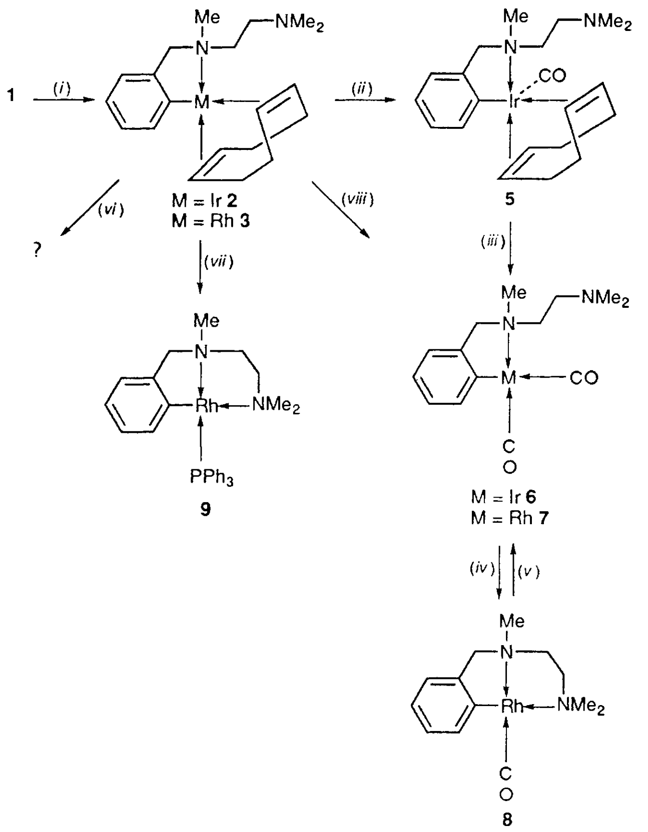
(*b*) Data collection and refinement	
T/K	295
Radiation, λ/Å	Mo-Kα (Zr-filtered), 0.710 73
$\theta_{min}, \theta_{max}$/°	1.23, 27.50
Scan type	$\omega/2\theta$
$\Delta\omega$/°	$1.23 + 0.35 \tan \theta$
Horizontal and vertical aperture/mm	3.4, 6.0
Distance of crystal to detector/mm	173
Reference reflections	2 2 0, 3 2 −2, −3 2 2
Data set	h 0–10, k −18 to 0, l 0–21
Total data	4901
Total unique data	2426 ($R_{int} = 0.013$)
Observed data	2078 [$I > 2.5\sigma(I)$]
No. of refined reflections, parameters	2078, 221
Final R, R', S	0.0284, 0.0308, 1.64
$(\Delta/\sigma)_{av,max}$ in final cycle	0.0488, 0.7045
Minimum, maximum residual electron density/e Å^{-3}	−0.69, 1.19 (Near Ir)

Table 2 Final atomic coordinates for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ir	0.072 33(4)	0.519 92(2)	0.358 82(2)
N(1)	0.088 2(10)	0.542 2(6)	0.222 1(4)
N(2)	−0.192 2(9)	0.595 7(6)	0.328 2(5)
C(1)	0.192 5(11)	0.648 1(6)	0.351 0(7)
C(2)	0.268 3(12)	0.671 1(8)	0.277 0(7)
C(3)	0.358 2(13)	0.753 9(9)	0.264 1(8)
C(4)	0.378 0(14)	0.817 7(9)	0.324 1(10)
C(5)	0.303 1(16)	0.801 0(8)	0.397 8(9)
C(6)	0.216 4(14)	0.719 4(7)	0.411 5(7)
C(7)	0.250 8(13)	0.594 8(10)	0.212 3(7)
C(8)	0.089(2)	0.459 3(8)	0.167 5(6)
C(9)	−0.052 4(14)	0.606 6(8)	0.196 9(6)
C(10)	−0.211 6(14)	0.582 5(9)	0.239 4(6)
C(11)	−0.340 0(13)	0.551 7(11)	0.366 2(7)
C(12)	−0.191 6(13)	0.696 9(8)	0.351 8(8)
C(13)	0.084 0(13)	0.512 0(7)	0.483 9(5)
C(14)	0.243 6(10)	0.488 2(7)	0.450 3(5)
C(15)	0.318 2(14)	0.388 6(8)	0.450 6(7)
C(16)	0.249(3)	0.328 5(11)	0.389 9(10)
C(17)	0.104(3)	0.367 8(8)	0.342 2(7)
C(18)	−0.058(2)	0.384 4(9)	0.374 2(8)
C(19)	−0.100(2)	0.370 0(12)	0.465 1(9)
C(20)	−0.033 5(15)	0.439 3(10)	0.521 1(7)

in Table 1. Final atomic coordinates are listed in Table 2. Neutral-atom scattering factors were taken from ref. 17 and corrected for anomalous dispersion.[18] All calculations were performed with SHELX 76[19] and PLATON[20a] (geometrical calculations and illustrations) on a DEC-5000 workstation; the figure was generated using ORTEP as implemented in PLATON.[20b]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

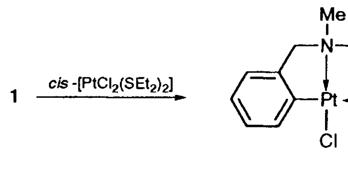


Scheme 1 Synthesis and chemistry of complexes **2** and **3**: (*i*) [{MCl(cod)}$_2$] (M = Rh or Ir); (*ii*) +CO, low temperature (M = Ir); (*iii*) +CO, −cod, room temperature (M = Ir); (*iv*) −CO (M = Rh); (*v*) +CO (M = Rh); (*vi*) +PPh$_3$ (M = Ir); (*vii*) +PPh$_3$ (M = Rh); (*viii*) +2CO, −cod, room temperature (M = Rh)

Results

The Monoanionic Ligand [$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2]$^-$.—The monoanionic potentially terdentate C,N,N′ ligand system [$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2]$^-$ (=L) is available from its dimeric organolithium complex [LiL]$_2$ **1**, whose preparation from the corresponding bromoaryldiamine and characterization are described elsewhere.[7b] Complex **1** is soluble in benzene, diethyl ether and tetrahydrofuran and is a good reagent for the introduction of this ligand system into transition-metal complexes where, as described in detail below, it provides an entry to new types of iridium(I), rhodium(I) and platinum(II) species.

Synthesis of [M^{I}L(cod)] (M = Ir **2** *or* Rh **3**) *and* [Pt^{II}Cl(L)] **4**.—The transmetallation reaction of [LiL]$_2$ **1** with [{MCl(cod)}$_2$] in a 1:1 molar ratio, see Scheme 1, readily affords the new square-planar iridium(I) and rhodium(I) complexes [M{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C*,*N*}(cod)] (M = Ir **2** or Rh **3**). The successful preparation of the platinum(II) complex [PtCl{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C*,*N*,*N*′}] **4** employs a 1:2 molar reaction of dimeric **1** with *cis*-[PtCl$_2$(SEt$_2$)$_2$], Scheme 2. From these reactions the complexes can be isolated as orange (**2** and **3**) and white (**4**) powders in high yield (81–97%). Like other cyclometallated iridium and rhodium



4

Scheme 2

complexes containing C,N chelating ligands, **2** and **3** have good solubility in benzene, toluene and dichloromethane, but are also moderately soluble in pentane and hexane. This latter solubility makes the work-up procedure more protracted than for analogous complexes of Ir and Rh;[5,21] instead of a simple precipitation and washing procedure, several trituration steps are needed to obtain good yields of the solid materials. Complexes **2** and **3** are extremely air-sensitive and upon exposure to air there is a rapid and distinct colour change to blue-purple.[5,9,21] Complex **4** is an air-stable solid which is moderately soluble in dichloromethane and poorly soluble in chloroform. The complexes have been characterized by ^{1}H, ^{13}C and two-dimensional COSY NMR spectroscopy, elemental analysis and for **2** an X-ray analysis.

Solid-state Structure of $[Ir\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}(cod)]$ **2**.—The crystal structure of [IrL(cod)] **2** is shown in Fig. 1 together with the adopted numbering scheme. Selected bond distances and bond angles are given in Table 3. The iridium centre in **2** is five-co-ordinated by the carbon atom of the aryl group C(1), the two nitrogen atoms of the terdentate ligand N(1) and N(2), and the two double bonds of the cod ligand m(1) and m(2) [midpoints of the double bonds C(13)–C(14) and C(17)–C(18), respectively]. The bond lengths involving iridium and carbon are in their normal ranges though the Ir(1)–N(1) distance of 2.279(7) Å is somewhat longer than normal.[5,21] For iridium(I) complexes containing bidentate C,N and cod ligands, a square-planar structure is normal. Bearing these points in mind we can now try to find a suitable description for the five-co-ordinate geometry of **2**. In **2**, C(1), N(1), m(1) and m(2) describe an approximate plane, but the interligand angles [for example, C(1)–Ir(1)–m(2) 162.6(5) and N(1)–Ir(1)–m(1) 154.9(3)°] show distortions that rule out a satisfactory description in terms of a square plane with N(2) in a pseudo-octahedral position; *cf.* the recently reported structure of the platinum(II) complex $[PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)]$.[22,23] A trigonal-bipyramidal geometry for **2** also does not fit, because the axial arrangement [C(1)–Ir(1)–m(2) 162.6(5)°] and the meridional interligand angles [N(1)–Ir(1)–N(2) 77.3(3), N(2)–Ir(1)–m(1) 125.5(3) and m(1)–Ir(1)–N(1) 154.9(3)°] are far from their expected values (78.2% distortion in the direction of a square-pyramidal geometry along the Berry pseudo-rotation coordinate).

The geometry of **2** can best be described as distorted square-pyramidal, with N(2) occupying the apical position and C(1), N(1), m(1) and m(2) forming the basal plane [deviations from the least-squares plane are 0.07(6), −0.06(5), −0.06(5) and 0.06(5) Å respectively], 0.37(5) Å above which the Ir atom lies. In this description the terdentate ligand $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]$ occupies three basal positions as is often seen in complexes of tripodal ligand systems.[1d,h,m,o–q] Although the Ir(1)–N(2) distance of 2.413(8) Å is very long, this can still be considered to be a co-ordinative interaction (with an empty hybrid orbital, probably p type, along the *z* axis); the lengthening is a result of the repulsive interaction between the nitrogen atom lone pair and the filled d_{z^2} orbital of the metal. For comparison, a Pd–N distance of 2.710(6) Å in the complex *trans*-$[PdBr(C_6H_4CH{=}NPh\text{-}C,N)(PPh_3)_2]$ has been suggested to represent a significant Pd–N interaction,[24] although normally Pd–N bonds are *ca.* 2–2.1 Å.[7a,25]

Finally, it is noted that the *N*Me atom of **2** is a stereogenic centre (Fig. 1 shows the *S* configuration); the unit cell only contains molecules of **2** with this configuration.

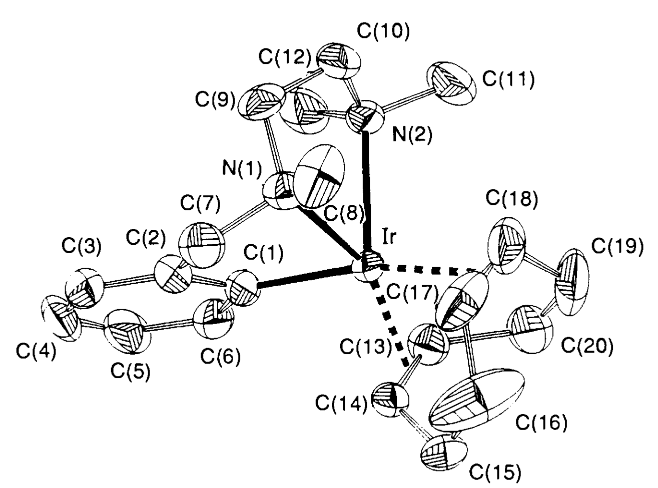


Fig. 1 ORTEP drawing of the molecular structure of complex **2** (drawn at 40% probability level), with the adopted atom labelling. Hydrogen atoms are left out for clarity

Table 3 Selected data on the geometry of complex **2** *

Ir–C(1)	2.048(9)	Ir–C(17)	2.175(12)
Ir–N(1)	2.279(7)	Ir–C(18)	2.188(14)
Ir–C(13)	2.067(8)	Ir–m(2)	2.064(13)
Ir–C(14)	2.081(8)	Ir–N(2)	2.413(8)
Ir–m(1)	1.948(9)		
C(1)–Ir–N(1)	77.9(4)	N(1)–Ir–m(2)	98.1(4)
C(1)–Ir–m(1)	90.6(4)	N(1)–Ir–N(2)	77.3(3)
C(1)–Ir–m(2)	162.6(5)	m(1)–Ir–m(2)	86.3(5)
C(1)–Ir–N(2)	90.2(3)	m(1)–Ir–N(2)	125.5(3)
N(1)–Ir–m(1)	154.9(3)	m(2)–Ir–N(2)	105.5(5)

* m(1) is the midpoint of C(13)–C(14), m(2) is the midpoint of C(17)–C(18).

Structure in Solution of [ML(cod)] (M = Ir **2** *or* Rh **3**) *and* [PtCl(L)] **4**.—Based on the combined NMR data for both **2** and **3** it can be concluded that in solution at room temperature these two d^8 metal complexes have a square-planar structure with bidentate C,N co-ordination of L and a non-co-ordinating NMe$_2$ group, *i.e.* $[M\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N\}(cod)]$ as depicted in Scheme 1; this situation contrasts with the five-co-ordinate structure of **2** in the solid state. For complex **4** the solution NMR data are consistent with a square-planar platinum(II) complex having terdentate co-ordination of the ligand L, *i.e.* $[PtCl\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N,N'\}]$ as depicted in Scheme 2.

The ^{1}H NMR spectra of complexes **2** and **3** are fairly similar (see Table 4). In the aromatic region there is a characteristic low-field doublet assigned to the proton *ortho* to the metal centre. The two benzylic protons, observed as an AB pattern, are diastereotopic and this is indicative for chelating co-ordination of the $C_6H_4CH_2NMe$ unit. In **3** only one of these protons shows a ^{103}Rh coupling [^3J(RhH) = 2 Hz] as is normal for this type of chelate ring.[21] Extra evidence for the co-ordination of the $C_6H_4CH_2NMe$ unit comes from the fact that the methyl group resonance is shifted to low field compared to the corresponding resonance of $PhCH_2N(Me)CH_2CH_2NMe_2$.[7a] The resonance of the enantiotopic Me groups of the NMe$_2$ unit in **2** and **3** is at almost the same position as that of this free parent aryldiamine. Therefore, in solution at room temperature this NMe$_2$ group is non-co-ordinating; in the case of NMe$_2$ co-ordination the Me groups would be diastereotopic. As a consequence of the NMe unit co-ordination in **2** and **3** the complexes are asymmetric with different chemical and magnetic environments above and below the co-ordination plane. This is certainly reflected in the AB pattern of the benzylic protons though, contrary to expectation, some of the four olefinic proton resonances of the cod ligand still overlap at 200 MHz; this feature was also seen for the olefinic cod protons in the asymmetric square-planar complexes [M{$C_6H_4CH_2NMe(Bu^t)$-2-*C,N*}(cod)] (M = Rh or Ir).[21]

In contrast to the similar ^1H NMR spectra of complexes **2** and **3**, their ^{13}C NMR spectra at room temperature do differ significantly from each other, but only as regards the cod signals (see Table 5). Characteristic similar resonances are (*i*) δ C_{ipso} at *ca.* 168 in the range expected for square-planar amino-chelated iridium and rhodium complexes[5,21] and (*ii*) the resonances of the $CH_2N(Me)CH_2CH_2NMe_2$ group. Compared to the ^{13}C data of the free parent aryldiamine $PhCH_2N(Me)CH_2CH_2NMe_2$ the benzylic and the NMe carbon signals are low-field-shifted (at δ *ca.* 73 and 49, respectively) whereas the methylenic (δ *ca.* 59) and the NMe_2 signals (at δ *ca.* 47) are little different.

For the rhodium complex **3** one does see the expected inequivalence of all carbon atoms of the cod ligand; four sharp signals for the aliphatic atoms (at δ *ca.* 30) and four sharp signals for the olefinic atoms at δ 68.5, 69.8, 89.3 and 92.7. The latter four are all coupled to ^{103}Rh, confirming the bidentate co-ordination mode of the cod ligand, and the $^1J(RhC)$ values of *ca.* 7 Hz on the low-field and of *ca.* 15 Hz on the high-field resonances are indicative for the olefinic moieties *trans* to a N atom and *trans* to a C atom, respectively.[5b] However, in the room-temperature ^{13}C NMR spectrum of the iridium complex **2** the olefinic C atom resonances are not apparent and the aliphatic C atoms afford two broad resonances at $\delta \approx 32$; this behaviour is explained below.

The ^1H NMR spectrum of the platinum complex **4** (see Experimental section) shows features similar to those of **2** and **3** concerning (*i*) the benzylic protons [AB pattern with only one resonance showing coupling to platinum [$^3J(PtH)$ = 106 Hz] and (*ii*) the Me group of the NMe unit (low-field shift at δ 2.91). The NMe unit is clearly co-ordinated and this is confirmed by the presence of platinum satellites on its signal with a $^3J(PtH)$ value of 49 Hz. This value lies in the range found for mutually *trans* N groups in platinum(II) complexes like *trans*-[Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$][25] and [PtX{$C_6H_3(CH_2NMe_2)_2$-2,6-*N,C,N′*}] (X = halide).[1c,f] The ^1H NMR spectrum of complex **4** in solution at room temperature shows, in contrast to the situation in **2** and **3**, that the NMe_2 unit is also co-ordinating. The NMe_2 unit affords diastereotopic Me resonances with shifts (δ 2.78 and 2.82) that are to low field of the NMe_2 resonance of $PhCH_2N(Me)CH_2CH_2NMe_2$. The shoulders on these resonances observed at 200 MHz are probably unresolved Pt satellites with $^3J(PtH)$ values of *ca.* 15 Hz; this would be consistent for a NMe_2 unit *trans* to a C atom in platinum(II) complexes.[26,27] Finally, in the aromatic region there is a characteristic low-field shifted doublet (with a ^{195}Pt coupling constant of 44 Hz) that can be assigned to the proton *ortho* to the platinum centre.

Fluxionality in Complexes **2** *and* **3**.—The ^{13}C NMR spectra of a solution of complex **2** in the temperature range 243–353 K show changes arising from fluxional behaviour during which it should be stressed that the Me groups of the NMe_2 unit remain enantiotopic.

From 213 to 243 K, there are four aliphatic cod signals and four olefinic signals, analogous to the situation for **3** found at room temperature. The high-field chemical shifts of two olefinic signals at δ 42.1 and 47.3 were established with a two-dimensional COSY NMR experiment carried out at 243 K; at this temperature the ^1H NMR spectrum shows four separate olefinic resonances. At 253 K the aliphatic and olefinic carbon resonances of cod are broadened. At 297 K, as mentioned above, the olefinic resonances are not apparent and there are two broad aliphatic resonances at $\delta \approx 32$. The latter sharpen upon raising the temperature (up to 353 K), but the olefinic resonances remain unobserved. With these results in mind, we also carried out variable-temperature NMR experiments with **3** and have found similar indications for fluxionality. However, the fluxional process now takes place at higher temperatures, that is to say: the ^{13}C NMR spectrum of **3** at 297 K shows the same resonance pattern as that of **2** at 213 K, the spectrum of **3** at 340 K is comparable to that of **2** at 297 and the spectrum of **3** at 360 K is comparable to that of **2** at 333 K.

Ligand Substitution Reactions in [ML(cod)] (M = Ir **2** *or* Rh **3**).—When CO is bubbled through a solution of the iridium complex **2** at 213 K, the five-co-ordinate monocarbonyl complex [Ir{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*}(cod)(CO)] **5** is formed quantitatively, see Scheme 1. This complex does not react further with CO at low temperature. However, bubbling CO through a benzene solution of **5** at room temperature does afford the new dicarbonyl complex [Ir{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*}(CO)$_2$] **6** and free cycloocta-1,5-diene. Attempts to isolate carbonyl complexes **5** and **6** failed.

Upon bubbling CO through a solution of the rhodium complex **3**, the dicarbonyl complex [Rh{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*}(CO)$_2$] **7** is obtained together with free cycloocta-1,5-diene, see Scheme 1. Complex **7** itself could not be isolated but work-up of a solution of **7** afforded the monocarbonyl complex [Rh{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N,N′*}(CO)] **8**, which was isolated in 95% yield as an air-sensitive, yellow-orange powder that is soluble in benzene and toluene. The dicarbonyl complex **7** can be reformed from the monocarbonyl complex **8** upon bubbling CO through its solution in benzene.

Table 4 Proton NMR data of the iridium and rhodium complexes **2**, **3** and **5**–**9**[a]

Complex[b]	Aryl H	$C_6H_4CH_2N$[c]	NMe	NMe_2	$(CH_2)_2$
2 [IrL(cod)][d]	7.67 (d)[e] 7.10–7.32 (m)	3.90 (d) 3.57 (d)	2.41 (s)	1.99 (s)	2.53–2.12 (m)
3 [RhL(cod)][f]	7.33 (d)[e] 7.06–7.24 (m)	3.77 (d) 3.46 (dd, 2)	2.24 (s)	1.92 (s)	2.88–1.83 (m)
5 [IrL(cod)(CO)][g,h]	7.85 (d)[e] 7.0–7.25 (m)	3.51 (d) 3.38 (d)	2.42 (s)	1.95 (s)	1.8–2.6 (m)
6 [IrL(CO)$_2$]	8.19 (d)[e] 7.05–7.22 (m)	3.60 (d) 3.45 (d)	2.49 (s)	1.85 (s)	2.25–2.8 (m)
7 [RhL(CO)$_2$][h]	8.00 (d)[e] 6.95–7.12 (m)	3.68 (d) 3.25 (d)	2.32 (s)	1.88 (s)	1.7–2.4 (m)
8 [RhL(CO)]	8.05 (dm)[e] 7.01 (d) 7.08–7.15 (m)	3.92 (d) 3.06 (dd, 2)	2.26 (s)	2.03 (s) 2.19 (s)	1.29 (t)[i] 1.35 (t)[i] 2.08 (td)[i,j] 2.37 (td)[i,j]
9 [RhL(PPh$_3$)][k]	7.76 (dd)[e,l] 6.9 (t)[e] 6.84 (d)[e] 6.55 (t)[e]	3.42 (dt, 3)[m] 4.54 (d)	2.49 (s)	1.47 (s) 2.04 (s)	1.43 (d)[j] 1.7 (d)[j] 2.32 (td)[i,j] 2.75 (td)[i,j]

[a] Recorded in C_6D_6 at room temperature unless otherwise stated; δ in ppm relative to external $SiMe_4$; $J(^{103}Rh^1H)$ in Hz in parentheses. [b] L = $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*. [c] AB pattern; $^2J(HH)$ 13–15 Hz. [d] δ[=CH(cod)] 3.63 (br t) and 3.76 (br t); both with double intensity. [e] $^3J(HH)$ 6–8 Hz. [f] δ[=CH(cod)] 4.03 (m), 4.16 (m) and 4.19 (br s) (double intensity). [g] In [$^2H_8$]toluene at −60 °C; δ[=CH(cod)] 4.06 (t), 4.23 (t) and 4.98 (t); the fourth resonance is obscured. [h] All resonances are broad. [i] $^3J(HH)$ 4 Hz. [j] $^2J(HH)$ 13 Hz. [k] δ 8.3 [t, H^2 and H^5 of Ph, $^3J(HH)$ 8, $^3J(PH)$ 8 Hz]. [l] $^4J(PH)$ 10 Hz. [m] $^4J(PH)$ 3 Hz.

Table 5 Carbon-13 NMR data of the iridium and rhodium complexes **2**, **3** and **7–9**[a]

	Aryl									
Complex	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C_6H_4CH	NMe	NMe_2	$(CH_2)_2$
2 [IrL(cod)][b]	169.8	150.1	123.7	121.3	125.8	134.9	74.4	49.7	47.6	60.4 59.6
3 [RhL(cod)][c]	166.8 (36.2)	149.2	123.7	121.8	125.2 (1.5)	133.9 (1.5)	72.0	48.2	46.2	59.4 58.7
4 [RhL(CO)$_2$][d]	169.6 (44.6)	150.6	122.4	126.2	124.2[e]	140.4 (4)[e]	72.4[e]	50.4[e]	47.6[e]	59.7[e] 58.9[e]
5 [RhL(CO)][f]	163.3 (40.5)	151.1	122.3	121.7	126.0 (3)	140.7 (5)	69.1 (1.5)	49.7	44.1 53.4	61.6 57.8
6 [RhL(PPh$_3$)][g]	163.9 (42)[h]	152.1	121.1	119.3	124.1	143.2 (3)[i]	70.4	47.8	45.2 51.3	64.1 58.0

[a] Recorded in C_6D_6 at room temperature; δ in ppm relative to $SiMe_4$; $J(^{103}Rh^{13}C)$ in Hz between parentheses. [b] δ[=CH(cod)] not observed. [c] δ[=CH(cod)] 68.5 (d, 15), 69.8 (d, 16), 89.3 (d, 6.5) and 92.7 (d, 7.5). [d] δ(CO) 193.3; ^1J(RhC) 55.6 Hz. [e] Broad. [f] δ(CO) 195.8; ^1J(RhC) 88.5 Hz. [g] δ(PPh$_3$); 140.5 [d, C_{ipso}, ^1J(PC) 33], 136.2 [d, C^2 and C^6, ^2J(PC) 13], 128.5 [d, C^4, ^4J(PC) 2] and 127.1 [d, C^3 and C^5, ^3J(PC) 9 Hz]. [h] dd, ^2J(PC) 15 Hz. [i] dd, ^3J(PC) 8 Hz.

The cod ligand in the rhodium complex **3** can also be replaced by a monodentate phosphine such as triphenylphosphine. The 1 : 1 reaction of **3** and PPh$_3$ affords in 90% yield [Rh{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N,N′*}(PPh$_3$)] **9**, which was isolated as a yellow powder, see Scheme 1.

The 1 : 1 reaction of complex **2** with PPh$_3$ does give a product which, unfortunately, we could not identify by ^1H NMR spectroscopy, but which is certainly not the Ir analogue of **9**.*

Complexes **5–9** have been characterized in solution by ^1H and ^{13}C NMR spectroscopy (see Tables 4 and 5, respectively) and the co-ordination mode of the ligand L identified unambiguously. Further identification of the carbonyl complexes was accomplished by IR spectroscopy and of the phosphine complex **9** by ^{31}P NMR spectroscopy (see Experimental section).

Characterization of Complexes **5–9**.—The ^1H NMR spectrum of the monocarbonyl complex [Ir(L-*C,N*)(cod)(CO)] **5** (243 K) resembles that of the starting material **2** but the aromatic doublet resonance is now more low field (δ 7.85) and only three inequivalent olefinic resonances are apparent. In the related complexes [Ir(L′-*C,N*)(cod)(CO)] (L′ = $C_6H_4CH_2NEt_2$-2, $C_6H_4CH_2NMe_2$-2 or 1-$C_{10}H_6NMe_2$-8) high-field shifts were established for olefinic protons by COSY NMR experiments,[27] and we therefore conclude that the fourth olefinic resonance is shifted to high field where it is obscured by the $(CH_2)_2$ and NMe_2 resonances. Based on its ^1H NMR spectrum, complex **5** is proposed to have a square-pyramidal structure as shown in Scheme 1, with the $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]^-$ and the cod ligands bidentate co-ordinated and the CO molecule in the axial position. Based on this structure the high-field shift of one olefinic proton is due to shielding effects of the aromatic ring. At temperatures above 273 K the ^1H NMR solution spectra of **5** indicate fluxionality; the benzylic protons are now enantiotopic (one broad singlet at δ 3.55) and two olefinic protons have become equivalent (one broad multiplet at δ 4.1). All other resonances are not significantly changed. These data point to a fluxional process for **5** that involves Ir–N(Me) dissociation/association ('off/on' movement, see below) and pyramidal inversion at the nitrogen atom. A similar process has been reported for the five-co-ordinate chiral organotin complexes [SnBrMe$_2${$C_6H_4CH(R)NMe_2$-2-*C,N*}] (R = Me, Et, Pr^i or Bu^t) which contain a bidentate C,N ligand.[28]

Based on spectroscopic data dicarbonyl complexes [M(L-*C,N*)(CO)$_2$] (M = Ir **6** or Rh **7**) have square-planar structures containing two *cis* carbonyl ligands, see Scheme 1, though complex **7** in solution exhibits fluxionality that is reflected in its IR and ^{13}C NMR spectra.

The *in situ* ^1H NMR data of **6** and **7** are very similar, though the resonances of **7** are all broadened. In both spectra there are signals of non-co-ordinated free cod at δ 2.2 and 5.5. The spectra show diastereotopic benzylic protons and for the NMe unit a low-field shift of the Me group that is typical for its N-co-ordination mode. The ^1H NMR data are also consistent with a non-co-ordinating NMe_2 group. In the aromatic region, the *ortho* proton appears as a doublet at δ *ca.* 8.1; this shift is to lower field than that of **5** (at δ 7.85) and might be due to deshielding effects of co-ordinated CO positioned as *cis* aryl–M–CO.[29] The IR spectrum of iridium complex **6** has absorptions at 1964 and 2038 cm^{-1} that can be assigned to the characteristic symmetric and antisymmetric CO stretches of a metal complex containing *cis*-positioned carbonyl ligands.[29,30]

The most important aspects of the ^{13}C NMR spectrum of **7** are: (*i*) all resonances, apart from some aromatic resonances, are broadened and (*ii*) there is only one doublet CO resonance, at δ 193.3 with a $J(^{103}Rh^{13}C)$ coupling constant of 56 Hz. This value would be typical for a bridging CO,[31] but this situation between two rhodium centres would afford a triplet resonance. Here intramolecular exchange between the two terminal CO ligands is affording the low value. Further evidence for such an exchange process comes from IR spectroscopy that has a much shorter time-scale than that of NMR spectroscopy. The IR spectrum of **7** shows no absorptions at *ca.* 1800 cm^{-1} that would be expected for a bridging CO,[32] but four terminal CO absorptions of which two at 1985 and 2040 cm^{-1} are comparable to those of **6**. The other two absorptions at 1933 and 2015 cm^{-1} are proposed to arise from an exchange process intermediate that has a five-co-ordinate geometry with terdentate C,N,N′ co-ordination of L.

The ^1H and ^{13}C NMR spectra of [Rh(L-*C,N,N′*)(CO)] **8** are characteristic for a square-planar ligand arrangement comprising terdentate co-ordination of L and a terminal CO. The Me groups of the NMe_2 unit are diastereotopic in both the ^1H and ^{13}C NMR spectra, and other signals are at similar positions to those found for **6** and **7**. The ^{13}C NMR spectrum of **8** shows the carbonyl group resonance at δ 195.8 with a ^1J(RhC) of 88.5 Hz and the single Rh–CO unit affords a single ν(CO) at 1932 cm^{-1} in its IR spectrum.

For complex **9**, [Rh{$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N,N′*}(PPh$_3$)], the spectroscopic data indicate that, as for **8**, that L is terdentate C,N,N′-co-ordinated (see Scheme 1) but now a phosphine instead of CO is *trans* to the NMe unit. In the ^1H NMR spectrum, the Me groups of the NMe_2 unit are diastereotopic with the rather high field position of one of these resonances (δ 1.47) being explained by shielding effects of the phosphine aromatic rings. The presence of co-ordinated PPh$_3$ is clearly shown in the ^1H NMR spectrum with a distinctive ^{31}P coupling constant on both the *ortho* proton and one of the benzylic protons of the terdentate ligand system. In the ^{13}C NMR spectrum coupling to ^{31}P is also seen on the resonances

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* To a solution of complex **2** (0.25 g, 0.51 mmol) in C_6H_6 (10 cm^3) was added a solution of PPh$_3$ (0.14 g, 0.53 mmol) in C_6H_6 (10 cm^3). After 1.5 h of stirring, the solution was evaporated *in vacuo* to an oily residue. This was washed with pentane (3 × 5 cm^3) to afford an orange powder. ^1H NMR (C_6D_6, 24 °C) δ 7.55 (m), 7.48 (br s, PPh$_3$), 7.0 (m, PPh$_3$), 3.95 (br), 3.35 (br), 2.7 (s), 2.5–1.3 (m) and 2.05 (s).

of the C_{ipso} and the *ortho* quaternary carbon atoms. The ^2J(PC) of 15 Hz on the former is indicative for a *cis* arrangement of C_{ipso} and the phosphine ligand; a *trans* C–M–P arrangement would give a value of *ca.* 100 Hz.[33] Consequently, the co-ordinated NMe_2 unit is, as expected, *trans* to C_{ipso} whose chemical shift of δ 163.9 is comparable to that of **8** which also has this C–M–NMe_2 arrangement. The presence of only one type of co-ordinated PPh_3 is clear from the ^{31}P NMR spectrum in which there is a single doublet resonance at δ 66.3 with a $J(^{103}Rh^{31}P)$ value of 244 Hz; the *trans* influence of the NMe unit is responsible for the rather high value of this coupling constant.

Discussion

The results of the present study clearly show that the ligand $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]^-$ (= L) developed by us is suitably designed for complexation to Ir^I, Rh^I and Pt^{II} [for its complexation to Pd^{II} and Pd^{IV} see ref. 7(*a*)]. There is also, it should be noted, a literature report that the closely related $[C_6H_4CH_2N(H)CH_2CH_2NMe_2\text{-}2]^-$ system can be used to stabilize W^{II}.[34] The following sections are used to discuss some aspects of the physical and chemical properties of the d^8 metal species containing L, with particular reference to the influences of the bi- (C,N) and ter-dentate (C,N,N′) co-ordination modes of this ligand.

Solid-state Structure of [IrL(cod)] **2**.—The crystal structure of complex **2** reveals a terdentate co-ordination mode of the ligand L in the solid state that leads to a complex with a five-co-ordinate geometry. With monodentate ligand systems mononuclear iridium(I) and rhodium(I) complexes[35] generally have four-co-ordinate square-planar structures,[36] but with polydentate ligand systems complexes with five-co-ordinate iridium(I) and rhodium(II) structures are not uncommon.[1d,h,m,o–q,37] In **2** the initial bidentate C,N co-ordination of L generates a situation in which the stereochemistry and flexibility of the $N(Me)CH_2CH_2NMe_2$ arm allows the terminal amine unit to attack the Ir centre perpendicular to the initially square co-ordination plane and this forces the cod ligand out of this plane. In this respect, **2** reflects the situation approaching the transition state on a reaction coordinate of attack of a nucleophile on a d^8 metal complex. Considering the space-filling model represented in Fig. 2, the iridium centre in **2** is, as it were, wrapped up in the C,N,N′-co-ordinated L and cod ligands so forming a kind of basket as in cyclodextrin chemistry.[38]

It is worthwhile emphasizing that $[C_6H_4CH_2N(Me)\text{-}CH_2CH_2NMe_2\text{-}2]^-$ has a completely different co-ordinating behaviour to that of the related potentially terdentate amine ligand system $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$. The iridium(I) and rhodium(I) complexes of this latter ligand, *i.e.* $[M\{C_6H_3(CH_2\text{-}NMe_2)_2\text{-}2,6\text{-}C,N\}(cod)]$, have square-planar structures in which the second amine functionality is non-co-ordinating.[5] Terdentate N,C,N′ co-ordination with this ligand is usually meridional, not pseudo-facial, and its inability in these species to provide five-co-ordinate complexes appears to be due to the low Lewis acidity of the late-transition metals, and potential steric hindrance between the unco-ordinated *ortho*-CH_2NMe_2 functionality and one of the double bonds of cod.

Fluxionality of [ML(cod)] *and* [PtCl(L)].—The five-co-ordinate solid-state structure of [IrL(cod)] **2** is not retained in solution. From solution NMR data the Ir^I centre has a square-planar environment and the complex is subject to fluxional behaviour; similar fluxionality is found for the rhodium complex **3**, though in another temperature range. There are two principal mechanisms one can invoke to explain this fluxionality: (*i*) rotation of the cod ligand around the metal–olefin axes or (*ii*) site exchange of the olefinic moieties of the cod ligand with or without association/dissociation of both amine units. Since the well known rotation of an olefin around a metal–olefin axis is generally restricted to monoolefins,[39,40] this would seem an unlikely mechanism for the bidentate, chelating cod ligand in **2** and **3**. Regarding the second mechanism, several complexes of rhodium and iridium have been reported to exhibit site exchange of cod olefinic moieties,[41] and it seems to be the appropriate choice for **2** and **3**. In this mechanism we propose a five-co-ordinate intermediate in which both nitrogen donor atoms of L are co-ordinated (observed in low-temperature NMR studies) rather than a three-co-ordinate intermediate in which both amine units are non-co-ordinated (no coalescence of the diastereotopic benzylic protons is observed up to 380 K). In this five-co-ordinate intermediate, site exchange of the olefinic moieties takes place *via* Berry pseudo-rotation processes.

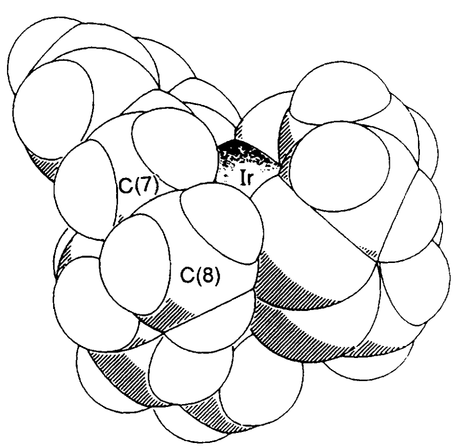

Fig. 2 Space-filling model of complex **2**

The fluxional process for **3** occurs at higher temperatures than for **2** and at room temperature the ^{1}H NMR data would seem to indicate that interaction of the terminal NMe_2 unit to the iridium centre in **2** is minimal. However, the low-temperature NMR data of **2** do point to a significant interaction of the free NMe_2 unit with the iridium centre even though the Me groups of the NMe_2 unit remain enantiotopic (*i.e.* eventual M–N dissociation/association processes and pyramidal inversion at nitrogen are still fast on the NMR time-scale). What one observes is significant high-field chemical shifts of one of the olefinic hydrogen and carbon atoms that can be most readily explained by an axial M–N interaction that forces the cod ligand out of the C,N co-ordination plane (as in the solid-state structure) and that puts one =C(H)– unit into the shielding influence of the aromatic ring system of L.

In contrast to complexes **2** and **3** the four-co-ordinate square-planar complex [PtCl(L)] **4** has a C,N,N′ terdentate co-ordination mode of $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]^-$. Because of our current interest in the characteristics and behaviour of intramolecular N–Pt bonds,[22,23] we have examined the ^{1}H NMR spectrum of [PtCl(L)] **4**, with particular regard to platinum–proton coupling constants, for extra insight into the ligand co-ordination. The data for the two benzylic protons [$^3J(^{195}PtH)$ = 106 and 0 Hz] are particularly instructive when combined with the crystal structure of [PdCl(L)],[7a] whose ^{1}H NMR spectrum closely resembles that of **4**. As is known for proton–proton coupling constants, vicinal coupling constants go through a minimum when the dihedral angle is 90°,[42] and the palladium structure has dihedral (torsion) angles $Pd\text{–}N_{Me}\text{–}C_{benzyl}\text{–}H$ of 163.90(50) and −75.20(50)° for the two benzylic protons.[7a] Considering the palladium complex as a model, we can conclude that in solution the five-membered chelate rings in [PtCl(L)] are 'locked' into one specific configuration with the larger dihedral angle affording the coupling constant of 106 Hz and the smaller angle (close to perpendicular) giving rise to minimal coupling to ^{195}Pt. This is a significantly different situation to that encountered in complexes of the related terdentate ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ {*e.g.* $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N'\}X]$ (X = halide)} where on the NMR time-scale there is concerted fast flipping of the two five-membered Pt–C–C–C–N rings and full equivalence of the benzylic protons.

Ligand Substitution Reactions in [ML(cod)] (M = Ir **2** *or* Rh **3**).—Carbon monoxide substitution of cod from iridium and rhodium complexes also containing either monodentate[43] or polydentate ligands[1a,30] is well known and almost invariably results in dicarbonyl species. In our work the bidentate chelating cod ligand in **2** or **3** is easily displaced by carbon monoxide to afford either the mono- or di-carbonyl complexes $[ML(CO)_{2-n}]$ (M = Ir, n = 0, **6**; M = Rh, n = 0, **7**; n = 1, **8**). Our observation at low temperature of the square-pyramidal CO-added complex [Ir(L-*C,N*)(cod)(CO)] **5**, wherein the cod ligand is still bidentate co-ordinated, is evidence that the substitution reaction is following an associative mechanism. At higher temperatures we believe that steric effects make the whole $N(Me)CH_2CH_2NMe_2$ arm non-co-ordinating and a four-co-ordinate metal species $[Ir\{C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C\}(cod)(CO)]$ is generated to which a second CO molecule can then co-ordinate. The following step, *i.e.* substitution of cod, is induced by reco-ordination of the bulky amine containing substituent and dicarbonyl complex **6** results. The formation of the rhodium dicarbonyl **7** from [RhL(cod)] is likely to be analogous. Further support for this 'arm-off–arm-on' mechanism comes from the results of the reactions of [Ir(L′-*C,N*)(cod)] (L′ = $C_6H_4CH_2NEt_2\text{-}2$, $C_6H_4CH_2NMe(Bu^t)\text{-}2$, $C_6H_4CH_2NMe_2\text{-}2$ and $1\text{-}C_{10}H_6NMe_2\text{-}8$) with CO;[21] the NMe_2 substituted ligands finally afforded the addition products [Ir(L′-*C,N*)(cod)(CO)], whereas the more sterically demanding ligands finally gave, through [Ir(L′-*C,N*)(cod)(CO)], the dicarbonyl complexes $[Ir(L'\text{-}C,N)(CO)_2]$. This type of mechanism has also been proposed for various CO addition reactions to complexes containing tripodal phosphine ligands,[1d,h,m,o,p] and reversible phosphine-arm dissociation was found in the reaction of the five-co-ordinate monocarbonyl complex $[RhH\{MeC(CH_2PPh_2)_3\}(CO)]$ with CO that affords $[RhH\{MeC(CH_2PPh_2)_3\}(CO)_2]$.[1q]

Comparison of the dicarbonyl complexes **6** and **7** shows that it is only the rhodium complex **7** that tends to form a five-co-ordinate species by terdentate C,N,N′ bonding of the ligand L. In such a species the distortion from square planar will be significant and this is more easily accommodated by rhodium than by iridium so that five-co-ordination is more preferred for the former.[36] However, with polydentate ligand systems Siegl *et al.*[1a,44] have shown that the opposite preference is also possible. An IR spectroscopic study of an equilibrium, comparable to that found for **7**, between a four- and five-co-ordinated dicarbonyl rhodium complex has been reported by Denise and Pannetier.[43d]

Underlying the chemistry of the rhodium and iridium carbonyl complexes are a number of other factors of which the nature of the metal centre and the ligand *trans* to C_{ipso} of L are the most important. For complexes **3** and **7**–**9** the electronic character of the *trans*-co-ordinated ligand is usefully indicated by the chemical shift data of the C_{ipso} atom, see Table 6, and the strong π acceptor CO correlates with the most low-field chemical shift. In these complexes one also sees that the nitrogen atom of the $CH_2CH_2NMe_2$ arm competes less well for the electron rich metal centres than CO does, and this is more pronounced for the iridium complexes where the metal centre is more nucleophilic than in the rhodium complexes.

Finally it is worth remarking that in the reactions of complexes **2** and **3** with carbon monoxide at atmospheric pressure, no CO insertion into the σ M–C_{ipso} bond was observed; five-co-ordinate complexes like **5** are frequently proposed as intermediates in CO insertion reactions under high CO pressure.[45]

Table 6 Chemical shift and ^1J(RhC) of C_{ipso} in the rhodium complexes **3** and **7**–**9**[a]

Complex	*trans* Ligand[b]	*cis* Ligand[c]	δ(C_{ipso})	$^1J(^{103}Rh^{13}C)$/Hz
3	C=C	C=C	166.8	36.2
7	CO	CO	169.6	44.6
8	N	CO	163.3	40.5
9	N	P	163.9	42.0

[a] Recorded in C_6D_6 at room temperature. [b] *trans*-Positioned to C_{ipso}. [c] *cis* Positioned to C_{ipso}; the other *cis* ligand is in all complexes the NMe group.

Conclusion

The *cis*-pincer ligand $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2]^-$ (= L) has been incorporated into complexes of Ir^I, Rh^I and Pt^{II} using the dinuclear lithium compound $[LiL]_2$ as reagent. In platinum complex [PtCl(L)] the ligand L is always terdentate C,N,N′ co-ordinated and conformationally rigid. However the behaviour and chemistry of [ML(cod)] (M = Ir or Rh) is based on primarily a bidentate C,N co-ordination mode that is supplemented by a tendency of the 'free' $CH_2CH_2NMe_2$ arm to interact with the metal centre. This latter interaction, clearly illustrated in the solid-state structure of square-pyramidal [IrL(cod)], leads to fluxional behaviour ('arm-off–arm-on' processes) in these complexes and affords anchimeric assistance in cod substitution reactions with CO and PPh_3.

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