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Synthesis and characterisation of 1-alkyl-2-imidazoline complexes of noble metals; crystal structure of *trans*-[$PtCl_2\{\overline{N{=}C(H)N(Et)CH_2CH_2}\}(PEt_3)$]*

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Treatment of a 1-alkyl-2-imidazoline $\overline{N(R)(CH_2)_2N{=}CH}$ with a μ-dichloro-dirhodium(I) or -diplatinum(II) complex $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ or $[\{Pt(\mu\text{-}Cl)Cl(PEt_3)\}_2]$ gave the mononuclear 1-alkyl-2-imidazoline complex $[RhCl\{\overline{N{=}C(H)N(R)CH_2CH_2}\}(cod)]$ (R = Et **1a** or CH_2Ph **1b**) or *trans*-$[PtCl_2\{\overline{N{=}C(H)N(R)CH_2CH_2}\}(PEt_3)]$ (R = Et **2a** or CH_2Ph **2b**) (cod = cycloocta-1,5-diene). A single-crystal X-ray diffraction study of **2a** revealed it to have a square-planar geometry about platinum, the imidazoline ring being coplanar with this plane, and a Pt–N distance of 2.088(11) Å; the Pt–P bond length of 2.231(4) Å indicates that the imidazoline ligand has a marginally stronger *trans* influence than analogues of its isomer such as $\overline{CN(R)(CH_2)_2NR}$. The rhodium complexes **1a** and **1b** have been shown to catalyse cyclopropanation of styrene and ethyl diazoacetate in high yields.

The co-ordination chemistry of imidazole and related compounds, including benzimidazoles, benzoxazoles and benzthiazoles, has been extensively studied in part because of their role in aspects of catalysis and biomimetics.[1,2] Since some of these heterocycles are corrosion inhibitors, their metal complexes may also have some relevance to anticorrosion mechanisms.[3] In addition, some have a variety of pharmacological effects, such as antitumour activity; for instance bis(acetato)bis(imidazole)-copper(II)[4,5] and imidazolium tetrachlorobis(imidazole)ruthenate(III)[6] were reported to be highly active antagonists toward tumour models. The presence of planar nitrogen-centred ligands L in *trans*-$[PtCl_2L_2]$ often appeared to enhance their cytotoxity relative to the corresponding *cis* isomer or to *cis*-$[PtCl_2(NH_3)_2]$.[7]

Imidazole and its derivatives are bound through N^3 of the imidazole ring.[8,9] However, conversion of an imidazolemetal complex into the isomeric (imidazolium ylide)metal complex, having a C^2–M bond, has been described.[10] In contrast, results on the related chemistry of 1-alkyl-4,5-dihydroimidazoles, the *N*-(or 1-)alkyl-2-imidazolines, are as yet much more sparse. At the outset of this work the only previous studies had been concerned with the bidentate imidazoline complexes of some late first-row transition metals.[11,12] Recently, the reaction of 2-phenylimidazoline with some palladium(II) complexes yielding cyclometallated products was described.[13]

In 1977 we reported that an attempt at an *in situ* synthesis of an NH-substituted imidazolidin-2-ylidene(or carbene)molybdenum(0) complex **I**, containing an $Mo\{\overline{CN(R)(CH_2)_2NH}\}$ moiety, from $[Mo(CO)_6]$, $CH(OMe)_2NMe_2$ and $H_2N(CH_2)_2NHR$ led instead to the isomeric *N*-bonded 2-imidazoline-molybdenum(0) complexes **II**;[14] the latter were also accessible from $[Mo(CO)_6]$ and $\overline{N(R)(CH_2)_2N{=}CH}$ (R = H or Et) as was $[RhCl\{\overline{N{=}C(H)N(R)CH_2CH_2}\}(cod)]$ from $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and $\overline{N(R)(CH_2)_2N{=}CH}$ (cod = cycloocta-1,5-diene). The present paper reports an extension of these experiments.

A further reason for our pursuing the present study is that the imidazoline complexes $[RhCl\{\overline{N{=}C(H)N(R)CH_2CH_2}\}(cod)]$ (R = Et **1a** or CH_2Ph **1b**) showed significant selective anti-

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bacterial activity[15] and were effective catalysts for cyclisation of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran.[16]

In this paper we describe the synthesis, isolation and spectroscopic characterisation of four new 1-alkyl-2-imidazoline complexes of rhodium(I) (**1a** and **1b**) and platinum(II) (**2a** and **2b**) derived from the imidazoline $\overline{N(R)(CH_2)_2N{=}CH}$ (R = Et or CH_2Ph) and the molecular structure of *trans*-$[PtCl_2\{\overline{N{=}C(H)N(Et)CH_2CH_2}\}(PEt_3)]$ **2a**, which we believe provides the first such data on a 1-alkyl-2-imidazolineplatinum(II) complex. The complexes **1a** and **1b** were shown to be effective catalysts for a cyclopropanation reaction.

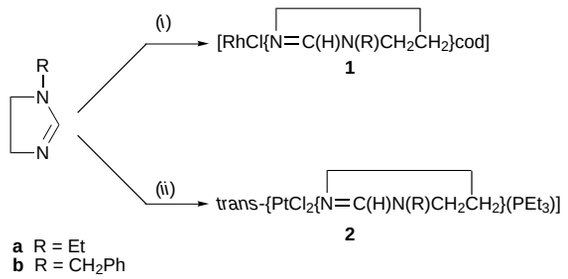
Results and Discussion

An enetetramine $[=\overline{CN(R)(CH_2)_2NR}]_2$ (abbreviated as $L^R{}_2$) has been shown to behave as a C-centred nucleophile in readily cleaving a di-μ-dichloro-dimetal complex such as $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ **A** or $[\{Pt(\mu\text{-}Cl)Cl(PEt_3)\}_2]$ **B** to give the imidazolidin-2-ylidene(or carbene)metal complex $[RhCl(cod)(L^R)]$ or $[PtCl_2(L^R)(PEt_3)]$.[17] A similar approach was used in the present study. Thus, 2 equivalents of the imidazoline $\overline{N(R)(CH_2)_2N{=}CH}$ (R = Et or CH_2Ph) were heated with **A** or **B** affording the appropriate mononuclear 1-alkyl-2-imidazoline-rhodium(I) **1** or -platinum(II) **2** complex in good yield (Table 1), Scheme 1 [(*i*) or (*ii*)].

Each of the complexes **1a**, **1b**, **2a** and **2b** was obtained in moderate to high yield as air-stable crystals, which were characterised by elemental analysis and IR (Table 1), ^1H NMR (Table 2) and ^{13}C-{^1H} NMR (Table 3) spectra; the tables also include corresponding data on the imidazolines $\overline{N(R)(CH_2)_2N{=}CH}$ [R = Et (an oil at ambient temperature) or CH_2Ph] which were reported briefly.[18]

* *Non-SI unit employed*: mmHg ≈ 133 Pa.

The IR spectra of each of the four complexes showed an intense absorption band at 1605 ± 12 cm^{-1} assigned to ν(C=N) which decreased in frequency relative to the free imidazolines in the case of **1a** and **1b**, while for **2a** and **3b** the opposite was the case, which may be because the ligand in the last two complexes is *trans* to a tertiary phosphine rather than an alkene, as in **1a** or **1b**.



Scheme 1 Routes to 1-alkyl-2-imidazoline complexes **1** and **2**: (*i*) [{Rh(μ-Cl)(cod)}$_2$] (0.5 equivalent), toluene, 110 °C, 2 h; (*ii*) [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] (0.5 equivalent), toluene, 110 °C, 2 h

The ^{1}H NMR spectral chemical shifts of the metal-bound imidazolines in complexes **1b** and **2b** were found at higher frequency than in the free imidazoline, but the effect was least obvious for the CH_2 protons and was not as marked as in the related imidazole complexes,[19] perhaps due to the aromaticity of the imidazole ligands. The variations in the ^{13}C NMR chemical shifts as between **1b** and **2b** on the one hand, and the free imidazoline on the other, were less pronounced.

The ^{13}C-{^{1}H} NMR spectra were particularly diagnostic as to the nature of the bonding in these new complexes, establishing them to be N^3-bound 2-imidazolines rather than C^2-bound imidazolidin-2-ylidenes. Thus, the imino N=CH signal was observed as a singlet at δ 161.3 for [RhCl{N=C(H)N(CH$_2$Ph)CH$_2$CH$_2$}(cod)] **1b**, but a doublet centred at δ 158.4 for *trans*-[PtCl$_2${N=C(H)N(CH$_2$Ph)CH$_2$CH$_2$}(PEt$_3$)] **2b**, $^4J(^{13}C–^{31}P) = 2$ Hz. By contrast, in $Rh^{I}–L^{R}$ or $Pt^{II}–L^{R}$ complexes, the carbene carbon atom showed a large $^{13}C–^{103}Rh$ or $^{13}C–^{195}Pt$ coupling constant, *e.g.* $^1J(^{13}C–^{103}Rh)$ in the range 38–65 Hz.[20]

The ^{31}P-{^{1}H} NMR spectra of complexes **2a** and **2b** showed singlets at δ 1.12 and 0.71 with ^{195}Pt satellites, $^1J(^{31}P–^{195}Pt) = 3345$ and 3314.1 Hz, respectively.

Table 1 Yields, melting points, IR [a] and analytical data for the new compounds

Compound	Yield (%)	M.p. (°C) [b.p. (°C, mmHg)]	ν(C=N)[a]/ cm^{-1}	Analysis (%)[b] C	H	N
N(Et)(CH$_2$)$_2$N=CH	90	[44–46, 0.5]	1605			
N(CH$_2$Ph)(CH$_2$)$_2$N=CH	84	39–40	1605	75.5 (75.0)	7.15 (7.5)	17.7 (17.5)
1a	95	112–113	1595	55.7 (54.4)	6.5 (6.0)	6.0 (6.7)
1b	72	120–121	1593	45.4 (45.3)	5.95 (6.4)	8.95 (8.15)
2a	62	92–93	1610	27.4 (26.9)	5.2 (5.25)	5.8 (6.15)
2b	88	103–104	1616	35.3 (34.9)	4.95 (4.8)	5.15 (5.7)

[a] As KBr discs. [b] Calculated values in parentheses.

Table 2 Proton NMR chemical shifts (δ) and coupling constants (*J*/Hz)

Compound	Ring C^{2}H	Ring 4,5-CH$_2$	Others
N(Et)(CH$_2$)$_2$N=CH	6.76 (s)	2.85 (m), 3.66 (m)	0.96 (t, $J = 7.0$, CH_2CH_3), 2.85 (q, $J = 6.0$, CH_2CH_3)
N(CH$_2$Ph)(CH$_2$)$_2$N=CH	6.70 (s)	2.70 (m), 3.70 (m)	3.67 (s, $CH_2C_6H_5$), 7.1 (m, $CH_2C_6H_5$)
1a	7.61 (s)	3.30 (t, $J = 11.4$), 3.47 (t, $J = 11.4$)	1.1 (t, $J = 7.25$, CH_2CH_3), 1.69 (d, $J = 4.9$), 2.23 (d, $J = 7.4$, cod CH_2), 3.14 (q, $J = 7.25$, CH_2CH_3), 3.79 (s) and 4.37 (s) (cod C=H)
1b	7.83 (s)	3.20 (t, $J = 10.7$), 3.51 (t, $J = 10.7$)	1.73 (d, $J = 8.6$), 2.39 (d, $J = 4.9$, cod CH_2), 3.82 (s) and 4.44 (s) (cod C=H), 4.29 (s, $CH_2C_6H_5$), 7.30 (m, $CH_2C_6H_5$)
2a	7.56 (s)	3.3 (t, $J = 10.0$), 4.0 (t, $J = 10.0$)	1.0 (t, $J = 7.0$, CH_2CH_3), 1.19 (t, $J = 7.6$, PCH_2CH_3), 1.80 (q, $J = 7.6$, PCH_2CH_3), 3.2 (q, $J = 7.0$, CH_2CH_3)
2b	7.78 (s)	3.3 (t, $J = 10.4$), 4.07 (t, $J = 10.4$)	1.20 (t, $J = 7.6$, PCH_2CH_3), 1.80 (q, $J = 7.6$, PCH_2CH_3), 4.33 (s, $CH_2C_6H_5$), 7.32 (m, $CH_2C_6H_5$)

Table 3 ^{13}C-{^{1}H} NMR chemical shifts (δ) and coupling constants (*J*/Hz)

Compound	Ring C^{2}H	Ring 4,5-CH$_2$	Others
N(Et)(CH$_2$)$_2$N=CH	157.2	42.3, 48.6	14.1 (CH_2CH_3), 55.8 (CH_2CH_3)
N(CH$_2$Ph)(CH$_2$)$_2$N=CH	157.2	48.6, 52.0	56.1 ($CH_2C_6H_5$), 127.6, 128.2, 128.9 ($CH_2C_6H_5$)
1a	161.1	30.2, 31.6	13.6 (CH_2CH_3), 41.8, 47.4 (cod CH_2), 50.7 (CH_2CH_3), 75.0 (d, $J = 14.4$) and 81.8 (d, $J = 11.7$) (cod CH)
1b	161.3	47.2, 50.9	30.1, 31.4 (cod CH_2), 51.3 ($CH_2C_6H_5$), 75.1 (d, $J = 13.0$) and 81.9 (d, $J = 11.0$) (cod CH), 127.7, 128.1, 128.8, 134.8 ($CH_2C_6H_5$)
2a	157.7	47.1, 50.7	7.4 (d, $J = 3.1$, PCH_2CH_3), 12.1 (CH_2CH_3), 13.8 (d, $J = 39.4$, PCH_2CH_3), 41.7 (CH_2CH_3)
2b	158.4	47.4, 51.2	7.6 (d, $J = 3.0$, PCH_2CH_3), 13.9 (d, $J = 39.0$, PCH_2CH_3), 51.6 ($CH_2C_6H_5$), 127.8, 128.1, 128.8, 134.8 ($CH_2C_6H_5$)

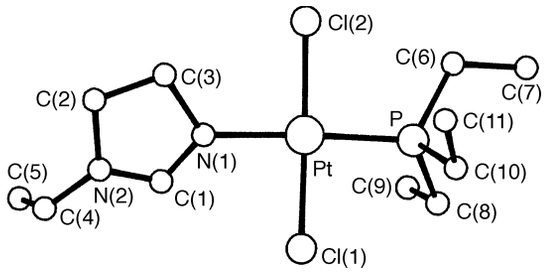


Fig. 1 Structure of *trans*-[$PtCl_2${N=C(H)N(Et)CH_2CH_2}(PEt_3)] **2a**

Table 4 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *trans*-[$PtCl_2$-{N=C(H)N(Et)CH_2CH_2}(PEt_3)] **2a**

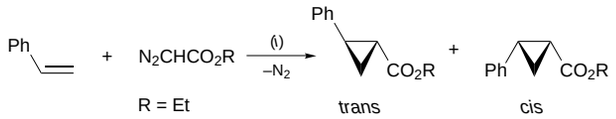
Pt–Cl(1)	2.283(4)	Pt–Cl(2)	2.291(5)
Pt–P	2.231(4)	Pt–N(1)	2.088(11)
P–C(6)	1.82(2)	P–C(8)	1.85(2)
P–C(10)	1.83(2)	N(1)–C(1)	1.29(2)
N(1)–C(3)	1.57(2)	N(2)–C(1)	1.33(2)
N(2)–C(2)	1.48(2)	N(2)–C(4)	1.41(2)
C(2)–N(3)	1.51(3)	C(4)–C(5)	1.52(2)
C(6)–C(7)	1.53(3)	C(8)–C(9)	1.56(2)
C(10)–C(11)	1.52(3)		
Cl(1)–Pt–Cl(2)	178.6(2)	Cl(1)–Pt–P	88.7(2)
Cl(1)–Pt–N(1)	88.6(3)	Cl(2)–Pt–P	92.5(2)
Cl(2)–Pt–N(1)	90.2(3)	P–Pt–N(1)	177.0(3)
Pt–P–C(6)	116.1(5)	Pt–P–C(8)	114.1(5)
Pt–P–C(10)	110.7(5)	C(6)–P–C(8)	105.3(7)
C(6)–P–C(10)	106.6(8)	C(8)–P–C(10)	102.9(7)
Pt–N(1)–C(1)	128.1(9)	Pt–N(1)–C(3)	124.8(9)
C(1)–N(1)–C(3)	107(1)	C(1)–N(2)–C(2)	109(1)
C(1)–N(2)–C(4)	125(1)	C(2)–N(2)–C(4)	124(1)
N(1)–C(1)–N(2)	116(1)	N(2)–C(2)–C(3)	104(1)
N(1)–C(3)–C(2)	103(1)	N(2)–C(4)–C(5)	116(1)
P–C(6)–C(7)	116(1)	P–C(8)–C(9)	111(1)
P–C(10)–C(11)	112(1)		

Single crystals of complex **2a** were grown from CH_2Cl_2–Et_2O at ambient temperature. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 4. The platinum is in a square-planar environment, with the chlorides *trans* to one another. The Pt–Cl [average 2.287(4) Å] and Pt–P [2.231(4) Å] bond lengths may be compared with those in *trans*-[$PtCl_2(L^{Ph})(PEt_3)$] **III** [L^{Ph} = CN(Ph)$(CH_2)_2$NPh]; Pt–Cl 2.301(6) (average) and Pt–P 2.291(4) Å].[21] Hence it appears that the *trans* influence of the 1-ethyl-2-imidazoline ligand in **2a** is slightly greater than that of the carbene (or imidazolidin-2-ylidene) ligand L^{Ph} in **III**.

For the cyclopropanation of alkanes with diazo compounds various efficient transition-metal catalysts have been reported. Although those available have proved useful in many instances, the search for alternatives goes on. Recently, bis(2-oxazolin-2-yl)(pyridine)ruthenium(II) complexes have been introduced as efficient cyclopropanation catalysts, which give good *trans–cis* selectivities.[22] Hence, we have checked the new rhodium(I) compounds **1a** and **1b** in the same context (Scheme 2).With 0.9 mol % catalyst at 80 °C styrene gave an excellent yield (91–95%) of the cyclopropanation product with ethyl diazoacetate. The mechanistic details of this catalytic reaction are currently under investigation.

Experimental

Unless otherwise stated, manipulations were carried out under argon using a high-vacuum manifold and conventional Schlenk techniques. Solvents were distilled over appropriate drying agents and thoroughly degassed prior to use. The complexes [{Rh(μ-Cl)(cod)}$_2$][23] and [{Pt(μ-Cl)Cl(PEt_3)}$_2$][24] were



Scheme 2 (*i*) Rhodium(I) complex **1a** or **1b**

prepared by published methods. The 1-alkyl-2-imidazolines N(R)$(CH_2)_2$N=CH (R = Et or CH_2Ph) were readily prepared from $CH(OMe)_2NMe_2$ and the appropriate diamine H_2N-$(CH_2)_2$NHR.[18]

The IR spectra were recorded as samples in KBr discs or as Nujol mulls on a Unicam 2100 grating spectrophotometer, NMR spectra, for samples in $CDCl_3$ solution, on a Bruker WM 360 or AC-250SY instrument. Elemental analyses were obtained in the Middle East Technical University, Ankara.

Preparations

1-Ethyl-2-imidazoline. A solution of *N*-ethylethane-1,2-diamine (12.55 g, 124 mmol) and $CH(OMe)_2NMe_2$ (19.06 g, 160 mmol) was slowly heated. When the oil-bath temperature reached 75–80 °C, NMe_2H and MeOH began to distil off. The brown residue was distilled at 34–36 °C (0.4 mmHg) to obtain a colourless liquid.

1-Benzyl-2-imidazoline. A solution of *N*-benzylethane-1,2-diamine (2.0 g, 13.3 mmol) in cyclohexane (4 cm^3) was added to $CH(OMe)_2NMe_2$ (1.29 g, 15 mmol) and the mixture was heated under distillation conditions, allowing the produced NMe_2H and MeOH to distil off. Then volatiles were removed under vacuum. The residue (1.79 g) was crystallised from toluene (1.5 cm^3)–hexane (6 cm^3).

(1-Alkyl-2-imidazoline)chloro(cycloocta-1,5-diene)rhodium(I) 1a and 1b. A solution of 1-ethyl-2-imidazoline (0.16 g, 1.6 mmol) in toluene (15 cm^3) and [{Rh(μ-Cl)(cod)}$_2$] (0.40 g, 0.80 mmol) was heated for 2 h under reflux. Hexane (5 cm^3) was added to the warm solution. Upon cooling to room temperature yellow-orange crystals of complex **1a** (0.47 g) were filtered off, washed with cold hexane (2 × 5 cm^3) and dried in a vacuum.

Similarly, from the same rhodium(I) starting material (0.60 g, 1.21 mmol) and 1-benzyl-2-imidazoline (0.38 g, 2.43 mmol), orange crystals of complex **1b** (0.89 g) were obtained.

***trans*-(1-Alkyl-2-imidazoline)dichloro(triethylphosphine)platinum(II) 2a and 2b.** A solution of 1-ethyl-2-imidazoline (0.14 g, 1.43 mmol) in toluene (10 cm^3) was added to [{Pt(μ-Cl)-Cl(PEt_3)}$_2$] (0.56 g, 0.73 mmol) and the mixture was heated for 2 h under reflux. Upon addition of hexane (6 cm^3) to the resulting yellow solution and cooling to room temperature, yellow crystals of complex **2a** (0.48 g) were filtered off, washed with hexane (2 × 10 cm^3) and dried under vacuum.

Yellow microcrystals of compound **2b** (0.56 g) were obtained similarly from 1-benzyl-2-imidazoline (0.20 g, 1.25 mmol) and the same platinum(II) starting material (0.50 g, 0.65 mmol).

Cyclopropanation reactions

In a typical experiment, the catalyst **1** (0.009 mmol) and styrene (20 mmol, 2.3 cm^3) were introduced into a Schlenk tube and then ethyl diazoacetate (1 mmol) in styrene (1 cm^3) was added. The mixture was stirred in an oil-bath at 80 °C for 4 h. The yields and the ratio of isomers were determined by GC.

Crystallography

Crystal data. $C_{11}H_{25}Cl_2N_2PPt$, M = 482.3, tetragonal, space group $I4$ (no. 82), $a = b$ = 20.997(2), c = 7.549(1) Å, U = 3327.9 $Å^3$, Z = 8, D_c = 1.93 g cm^{-3}, $F(000)$ = 1856, μ(Mo-Kα) = 89.2 cm^{-1}, 293 K.

Data collection, structure solution and refinement. X-Ray diffraction data were collected on a crystal of dimensions 0.3 × 0.2 × 0.2 mm, in a Lindemann capillary sealed under argon, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with a scan width of $\Delta\theta = (0.8 + 0.35 \tan\theta)°$, maximum scan time of 1 min and Mo-Kα radiation (λ = 0.710 69 Å). A total of 1112 unique reflections was measured for $2 < \theta < 22°$ and $+h +k +l$; 1010 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]/L_p$, were used in the refinement. There was no crystal decay during the data collection. A correction (maximum 1.22, minimum 0.85) for absorption was applied using DIFABS[25] after isotropic refinement.

The structure was solved using the heavy-atom routines of SHELX 86[26] and non-hydrogen atoms were refined on F with anisotropic thermal parameters by full-matrix least squares. Hydrogen atoms were held at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. Final parameters were $R = 0.026$, $R' = 0.033$, $S = 1.26$, 154 variables, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.01$ and $(\Delta\rho)_{max,min}$ +0.57, −0.65 e Å^{-3} on a final difference map. Programs from the SDP-PLUS package[27] were run on a Micro Vax II computer.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/428.

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References

1 A. L. Abuhijleh, *Polyhedron*, 1996, **15**, 285.
2 K. Nonoyama, W. Mori and M. Nonoyama, *Polyhedron*, 1994, **13**, 891; S. Bennett, S. M. Brown, G. Conole, M. Kessler, S. Rowling, E. Sinn and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 1995, 367.
3 G. Xue, Q. Dai and S. Jiang, *J. Am. Chem. Soc.*, 1988, **110**, 2393; G. Xue, S. Jiang, X. Huang, G. Shi and B. Sun, *J. Chem. Soc., Dalton Trans.*, 1988, 1487.
4 J. R. J. Sorrenson, *Prog. Med. Chem.*, 1989, **26**, 437.
5 H. Tamura, H. Imai, J. Kuwahara and Y. Sugiura, *J. Am. Chem. Soc.*, 1987, **109**, 6870.
6 A. Galeano, M. R. Berger and B. K. Keppler, *Arzneim.-Forsch., Drug Res.*, 1992, **42**, 821.
7 M. van Beusichem and N. Farrell, *Inorg. Chem.*, 1992, **31**, 634.
8 R. J. Sundberg, R. F. Bryan, I. F. Taylor and H. Taube, *J. Am. Chem. Soc.*, 1974, **96**, 381.
9 J. Müller and R. Stock, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 993.
10 F. Bonati, L. A. Oro, M. T. Pinillos and C. Tejel, *J. Organomet. Chem.*, 1994, **465**, 267.
11 S. S. Tandon, L. K. Thompson, J. N. Bridson and J. C. Dewan, *Inorg. Chem.*, 1994, **33**, 54 and refs. therein.
12 J. Bremer, S. Uhlenbrock, A. A. Pinkerton and B. Krebs, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1183.
13 C. Navarro-Ranninger, F. Zamora, I. López-Solera, A. Monge and J. R. Masaguer, *J. Organomet. Chem.*, 1996, **506**, 149.
14 P. B. Hitchcock, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2160.
15 B. Çetinkaya, E. Çetinkaya, H. Küçükbay and R. Durmaz, *Arzneim.-Forsch., Drug Res.*, 1996, **46**, 821.
16 B. Çetinkaya, I. Özdemir, C. Bruneau and P. H. Dixneuf, unpublished work.
17 M. F. Lappert, *J. Organomet. Chem.*, 1988, **358**, 185.
18 E. Çetinkaya and M. F. Lappert, *Chemistry and Chemical Engineering Symposium, Abstracts, Kusadasý*, 1989, p. 140.
19 F. Bonati, L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem.*, 1989, **369**, 253.
20 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, D. B. Shaw, K. Spyropoulos and N. J. W. Warhurst, *J. Organomet. Chem.*, 1993, **459**, 311.
21 L. Manojlović-Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1974, 2427.
22 S.-B. Park, N. Sakata and H. Nishiyama, *Chem. Eur. J.*, 1996, **3**, 303; H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki and K. Itoh, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1247.
23 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
24 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2351.
25 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A.*, 1983, **39**, 158.
26 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structure Refinement, University of Göttingen, 1986.
27 SDP-PLUS, Enraf-Nonius, Delft, 1978.

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