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First intramolecular aromatic substitution by gold(III) of a ligand other than pyridine derivatives. Synthesis and crystal structure of the novel five-membered cycloaurated complex of 1-ethyl-2-phenylimidazole

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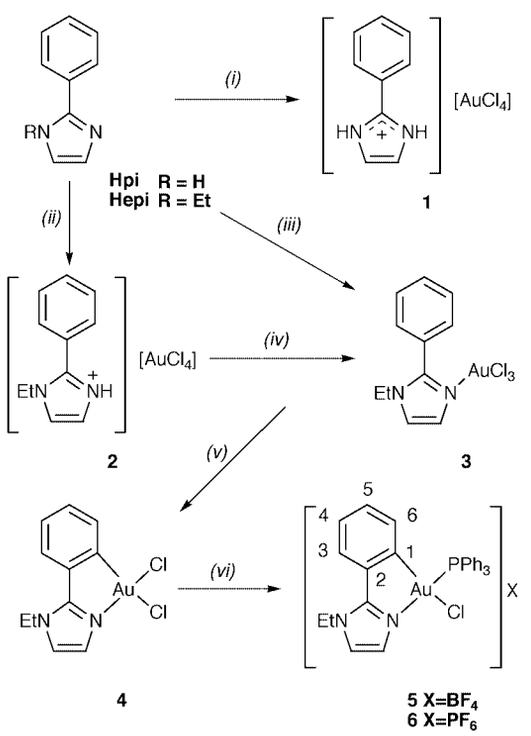
Reactions of gold(III) compounds, $AuCl_3·4H_2O$ and $HAuCl_4·4H_2O$, with 2-phenyl-1*H*-imidazole (Hpi) and 1-ethyl-2-phenylimidazole (Hepi) have been performed under various reaction conditions: Hpi afforded only the salt [H(Hpi)][$AuCl_4$], while Hepi produced both the salt [H(Hepi)][$AuCl_4$] and the adduct [$AuCl_3$(Hepi)]. Cycloauration of Hepi, the first example of cycloauration of a substrate other than pyridine derivatives, has been established by the formation of [$AuCl_2$(epi-C^1,N)] [epi = 2-(1-ethyl-2-imidazolyl)phenyl] from the reaction between the adduct [$AuCl_3$(Hepi)] and $AgBF_4$. The cyclometallated structure of Hepi has been confirmed by the X-ray crystallographic study of a derivative [AuCl(epi-C^1,N)(PPh_3)]PF_6.

Cyclometallation proceeds *via* direct C–H bond activation of a heterosubstituted molecule to form a chelate ring composed of a co-ordination bond and a covalent metal–carbon bond.[1] This method of formation of a M–C σ bond is more convenient than the classical one using organomagnesium or organolithium compounds. Compared with the extensively studied cyclopalladation or cycloplatination, the chemistry of cycloauration has not been investigated so much.[2] The first cycloauration was performed in 1989 by Constable and Leese[3] using 2-phenylpyridine. Thereafter in this decade cycloaurated complexes formed by C–H bond activation of the following substrates have been reported: 2,9-diphenyl-1,10-phenanthroline,[4] 4-(4-methoxyphenyl)-6-phenyl-2,2′-bipyridine,[5] 2-benzylpyridine,[6] 6-benzyl-2,2′-bipyridine,[7] 6-*tert*-butyl-2,2′-bipyridine,[7] 2-benzoylpyridine,[8] 2-anilinopyridine,[9,10] 2-phenoxypyridine,[10] 2-(phenylsulfanyl)pyridine,[10] 2-(alkylsulfanyl)pyridine,[11] papaverine (1-[(3,4-dimethoxyphenyl)-methyl]-6,7-dimethoxyisoquinoline),[12] 2-(2-thienyl)pyridine[13] and 2-(3-thienyl)pyridine.[13] Recently, in connection with the antitumor and luminescence properties of some cycloaurated complexes, much more interest has been paid to the chemistry of cycloauration. However, as shown above all the substrates which underwent intramolecular C–H bond activation by gold(III) are definitely limited to pyridine derivatives. In order to break through this situation we have set out to investigate the cycloauration of 2-phenylimidazole derivatives. Here we report the first successful intramolecular aromatic substitution of a substrate other than pyridine derivatives by gold(III), *viz*. cycloauration of 1-ethyl-2-phenylimidazole, and also the crystal structure of a derivative [AuCl(epi-C^1,N)(PPh_3)]PF_6 [epi = 2-(1-ethyl-2-imidazolyl)phenyl].

Results and discussion

The methods for preparation of the new gold(III) complexes derived from 2-phenyl-1*H*-imidazole (Hpi) and 1-ethyl-2-phenylimidazole (Hepi) are shown in Scheme 1. Assignment of the ^{1}H NMR spectra was performed with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY) and the data are summarized in Table 1.



Scheme 1 (*i*) $AuCl_3·4H_2O$ or $\frac{1}{2}HAuCl_4·4H_2O$; (*ii*) $AuCl_3·4H_2O$; (*iii*) $\frac{1}{2}HAuCl_4·4H_2O$; (*iv*) CH_3CN–water (1 : 5); (*v*) $AgBF_4$; (*vi*) PPh_3, $NaBF_4$ (**5**) or NH_4PF_6 (**6**).

Synthesis and characterization of the gold(III) complexes of Hpi and Hepi

The reaction of $AuCl_3·4H_2O$ with an equimolar amount of 2-phenyl-1*H*-imidazole (Hpi) or 1-ethyl-2-phenylimidazole

Table 1 Proton NMR spectral data of the new gold(III) complexes[a]

Complex	Imidazolyl moiety[b]			Benzene ring[b]		Phosphine
	$H^{4'}$ or $H^{5'}$	CH_2	CH_3			
1 [H(Hpi)][$AuCl_4$]	7.81 (s, 2 H)	—	—	8.0 (m, 2 H, *o*-H)	7.66 (m, 3 H, *m*, *p*-H)	—
2 [H(Hepi)][$AuCl_4$]	7.97 (d),[c] 7.86 (d)[c]	4.17 (q)[d]	1.38 (t)[d]	7.8–7.65 (m, 5 H)		—
3 [$AuCl_3$(Hepi)]	7.91 (d),[c] 7.78 (d)[c]	4.05 (q)[d]	1.30 (t)[d]	7.75–7.7 (m, 5 H)		—
4 [$AuCl_2$(epi-C^1,*N*)]	7.77 (d),[c] 7.56 (d)[c]	4.52 (q)[d]	1.46 (t)[d]	7.85 (d, 1 H)[e] 7.48 (t, 1 H)[e]	7.68 (d, 1 H)[e] 7.34 (t, 1 H)[e]	—
5 [AuCl(epi-C^1,*N*)(PPh_3)]BF_4	7.5–7.9 (c, 2 H)[f]	4.57 (q)[d]	1.47 (t)[d]	7.5–7.9 (1 H, H^3)[f] 6.78 (t, 1 H, H^5)[e]	7.34 (br t, 1 H, H^4)[e] 6.62 (br d, 1 H, H^6)[e]	7.5–7.9 (c, 15 H)
6 [AuCl(epi-C^1,*N*)(PPh_3)]PF_6	7.6–7.95 (c, 2 H)[f]	4.55 (q)[d]	1.48 (t)[d]	7.6–7.95 (1 H, H^3)[f] 6.78 (t, 1 H, H^5)[e]	7.34 (t, 1 H, H^3)[e] 6.60 (br d, 1 H, H^6)[e]	7.6–7.95 (c, 15 H)

[a] Measured in DMSO-d_6 at 270 MHz and at 23 °C; δ in ppm with respect to $SiMe_4$; s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, c = complex. [b] For numbering see Scheme 1. [c] ^3J(HH) = 2.0 Hz. [d] ^3J(HH) = 7.3 Hz. [e] ^3J(HH) = 8.0 Hz. [f] Overlapping with triphenylphosphine signals.

(Hepi) carried out in dichloromethane did not afford the addition complex [$AuCl_3$(L)] (L = Hpi or Hepi), giving only the corresponding salt [H(Hpi)][$AuCl_4$] **1** or [H(Hepi)][$AuCl_4$] **2**, respectively. It is not clear whether the hydrated water molecule in $AuCl_3 \cdot 4H_2O$ is the proton source for the formation of the salts, but a similar result has been reported for the synthesis of 2-(α,α-dimethylbenzyl)pyridinium tetrachloroaurate(III) from the reaction between 2-(α,α-dimethylbenzyl)pyridine and $AuCl_3 \cdot 2H_2O$.[6] Previously, we achieved the conversion of the tetrachloroaurate salts of 2-phenoxy- and 2-(phenylsulfanyl)-pyridine into corresponding adducts in acetonitrile–water (1 : 5) mixed solvent.[10] The addition complex [$AuCl_3$(Hepi)] **3** was obtained by the above method and also by the reaction of $HAuCl_4 \cdot 4H_2O$ with two molar equivalents of Hepi in ethanol. However, in the case of Hpi the corresponding adduct [$AuCl_3$(Hpi)] could not be prepared by either method, recovering or forming only the salt **1**, implying the higher stability of the 2-phenylimidazolium cation.

Different from the chemical behavior of the adducts of 2-phenoxy- and 2-(phenylsulfanyl)-pyridine,[10] the adduct of Hepi **3** did not change into the corresponding cycloaurated complex [$AuCl_2$(epi-C^1,*N*)] [epi = 2-(1-ethyl-2-imidazolyl)-phenyl] **4** by heating in acetonitrile–water (1 : 5) solvent. The novel cycloaurated complex **4** was finally obtained in 20% yield when the adduct **3** was refluxed with $AgBF_4$ in CH_2Cl_2. However, the yield of **4** did not increase under several reaction conditions using other silver salts such as AgO_2CMe and AgO_2CCF_3 in the presence or absence of Na_2CO_3 in CH_2Cl_2 or acetone. This is the first example of intramolecular aromatic substitution of a ligand other than pyridine derivatives, which we believe could throw new light upon the development of cycloauration chemistry. It should be added that by transmetallation from the corresponding organomercury(II) compounds or by bromination of gold(I) complexes, [AuBr(L)] [L = $PPh_2(C_6H_4CH{=}CH_2)$ or $PPh_2(C_6H_4CH_2CH{=}CH_2)$], cycloaurated complexes of azobenzene,[14,15] benzylamine,[15–17] 2-phenyloxazoline,[17] benzylideneamine[18] and diphenylphosphine[19] derivatives have been prepared.

In the ^{1}H NMR spectrum of complex **4** two imidazole-ring protons resonated as an AB quartet at δ 7.56 (d) and 7.77 (d). It has been reported that gold(III) sometimes attacks on carbon atoms in heterocycles rather than those in the benzene ring, *e.g.*, C-4 metallation of the pyrazole ring in 1-phenylpyrazole[20] or C-5 auration of the thiophene ring in 2-(2-thienyl)pyridine[13] or 6-(2-thienyl)-2,2′-bipyridine.[21] However, in complex **4** the detection of two imidazole-ring protons completely excludes the possibility of formation of aurated imidazole species. On the contrary, the benzene-ring protons of **4** appeared as a well separated ABCD pattern typical for an *o*-phenylene group (Table 1). On the basis of these results it was concluded that in complex **4** metallation occurs at the *ortho* position of the phenyl ring of Hepi, forming a cycloaurated chelate ring. As expected from the cycloaurated structure, the far-IR spectrum of **4** showed two bands at 351 and 296 cm^{-1} characteristic of ν(Au–Cl) frequencies *trans* to the imidazolyl nitrogen atom and *trans* to the phenylene carbon atom, respectively.[18]

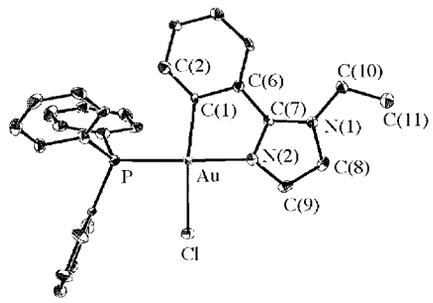


Fig. 1 An ORTEP view of complex [AuCl(epi-C^1,*N*)(PPh_3)]PF_6 **6** (molecule A). Hydrogen atoms and the hexafluorophosphate anion are omitted for clarity.

Synthesis and structural analysis of [AuCl(epi-C^1,*N*)(PPh_3)]PF_6

Complex **4** reacted with an equimolar amount of PPh_3 in the presence of an excess of $NaBF_4$ or NH_4PF_6 to give cationic complexes **5** (Λ_M 138 S cm^2 mol^{-1} in acetone) or **6** (Λ_M 141 S cm^2 mol^{-1} in acetone), respectively. The IR spectra of **5** and **6** exhibited only one band assignable to the ν(Au–Cl) frequency *trans* to the phenylene group at 315 and 311 cm^{-1}, respectively,[18] besides a strong band due to counter anion at 1055 (**5** BF_4^-) and 834 cm^{-1} (**6** PF_6^-). In the ^{1}H NMR spectrum of **5** and **6** the H^6 signal appeared at considerably higher field [δ 6.62 (**5**), 6.60 (**6**)] which is caused by the ring current of the adjacent benzene ring of the triphenylphosphine co-ordinated *cis* to the C–Au bond. On the basis of these data together with elemental analysis, **5** and **6** were assigned to cationic four-co-ordinate complexes [AuCl(epi-C^1,*N*)(PPh_3)]BF_4 and [AuCl(epi-C^1,*N*)-(PPh_3)]PF_6, respectively.

The structure of complex **6** was established by X-ray diffraction. The crystal consists of two crystallographically independent molecules A and B, the structures of which are almost identical. Selected bond distances and angles are summarized in Table 2. Fig. 1 shows an ORTEP[22] view of the cationic moiety of the molecule A. In molecules A and B the gold atoms have essentially square-planar AuCNClP co-ordination with the mean deviation from the best planes of 0.1016 and 0.1264 Å, respectively. The Au–C and Au–P bond distances in **6** are as in other gold(III) complexes.[4,6–8,10,17,18,23] The bite angle of the cycloaurated ligand is 80.8(2)° (molecules A and B), whose value is comparable to those in five-membered auracycles derived from 4,4′-dimethylazobenzene [80.1(2)°],[24] 4-butyl-*N*-(trimethoxybenzylidene)-aniline [81.41(14)°],[18] 4,4-dimethyl-2-phenyl-1,3-oxazoline

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **6**

	Molecule A	Molecule B
Au–C(1)	2.049(6)	2.055(6)
Au–N(2)	2.045(5)	2.047(5)
Au–Cl	2.365(1)	2.362(1)
Au–P	2.300(2)	2.307(2)
C(1)–C(6)	1.422(8)	1.431(7)
C(6)–C(7)	1.461(8)	1.446(8)
C(7)–N(2)	1.342(8)	1.340(8)
N(2)–C(9)	1.367(7)	1.391(7)
C(9)–C(8)	1.369(8)	1.360(8)
C(8)–N(1)	1.390(8)	1.379(7)
N(1)–C(7)	1.362(7)	1.347(7)
C(1)–Au–N(2)	80.8(2)	80.8(2)
C(1)–Au–P	95.9(2)	96.4(2)
N(2)–Au–P	172.7(1)	167.3(1)
P–Au–Cl	93.26(6)	93.83(6)
N(2)–Au–Cl	90.6(1)	90.4(1)
C(1)–Au–Cl	169.1(2)	168.3(2)

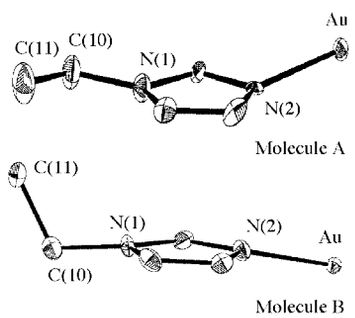


Fig. 2 Orientation of ethyl group in molecules A and B of complex **6**.

[81.7(3)°][17] and *N*,*N*-dimethylbenzylamine [82.2(4)°],[25] and smaller than the values found in the six-membered auracycles [AuCl($C_6H_4NHC_5H_4N$-C^1,*N*)(PPh_3)]BF_4 [85.2°],[10] [$AuCl_2$($C_6H_4CMe_2C_5H_4N$-C^1,*N*)] [85.7(1)°],[7] [AuCl($C_6H_4CH_2C_5H_4N$-C^1,*N*)(PPh_3)]BF_4 [85.8(4)°],[8] [$AuCl_2$($C_6H_4OC_5H_4N$-C^1,*N*)] [86.6°],[10] [$AuCl_2$($C_6H_4SC_5H_4N$-C^1,*N*)] [88.3°][10] and [$AuCl_2$-($C_6H_4COC_5H_4N$-C^1,*N*)] [89.5(3)°].[8] The slightly longer Au–Cl [2.365(1) (molecule A) and 2.362(1) Å (molecule B)] and Au–N bond distances [2.045(5) (molecule A) and 2.047(5) Å (molecule B)] are caused by the greater *trans* influences of the carbon donor and phosphine ligand, respectively. In the chelated epi moiety the plane of benzene ring slightly twists against the plane of imidazole, resulting in dihedral angles of 16.4 (molecule A) and 16.7° (molecule B). The main difference between molecules A and B is the orientation of the ethyl group in the imidazole ring as shown in Fig. 2: in molecule A the plane composed of N(1), C(10) and C(11) is nearly co-planar with the best plane of the imidazole ring (dihedral angle 5.4°), while in B the plane is nearly perpendicular to the imidazole ring (dihedral angle 90.8°).

Experimental

General

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, ^{1}H NMR spectra on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. Conductivity measurements were carried out at 25 °C on a Toa Electronics CM-20E conductometer. 1-Ethyl-2-phenylimidazole[26] was prepared according to the literature. Other reagents were obtained commercially and used without purification.

Syntheses

[H(Hpi)][$AuCl_4$] 1. *Method (a).* A dichloromethane (10 cm^3) solution of 2-phenylimidazole (0.083 g, 0.576 mmol) was added to a solution of $AuCl_3$·$4H_2O$ (0.214 g, 0.569 mmol) in the same solvent (10 cm^3). After the resulting mixture was stirred overnight at room temperature, it was evaporated to dryness and the residue extracted with acetonitrile. The extract was concentrated under reduced pressure and diluted with diethyl ether to give yellow microcrystals of complex **1** (0.125 g, 45%), mp 210 °C (Found: C, 22.5; H, 1.9; N, 5.65. $C_9H_8AuCl_4N_2$ requires C, 22.4; H, 1.65; N, 5.8%); ν_{max}/cm^{-1} (KBr) 3290 (br, NH) and 359 (Au–Cl); Λ_M(1 × 10^{-3} M, acetone) 152 S cm^2 mol^{-1}.

Method (b). An ethanol (3 cm^3) solution of 2-phenylimidazole (0.147 g, 1.02 mmol) was added to a solution of $HAuCl_4$·$4H_2O$ (0.205 g, 0.498 mmol) in the same solvent (5 cm^3). The resulting yellow solution was stirred at room temperature for 20 h. After similar work-up to that described in method (a), complex **1** was obtained in 36% yield.

[H(Hepi)][$AuCl_4$] 2. A dichloromethane (20 cm^3) solution of 1-ethyl-2-phenylimidazole (0.059 g, 0.343 mmol) was added to a solution of $AuCl_3$·$4H_2O$ (0.110 g, 0.292 mmol) in the same solvent (20 cm^3) and the resulting mixture stirred at room temperature. After 12 h the yellow solution was concentrated and diluted with hexane to give yellow microcrystals of complex **2** (0.077 g, 55%), mp 116 °C (Found: C, 26.15; H, 2.6; N, 5.5. $C_{11}H_{13}AuCl_4N_2$ requires C, 25.8; H, 2.55; N, 5.45%); ν_{max}/cm^{-1} (KBr) 367 (Au–Cl); Λ_M(1 × 10^{-3} mol dm^{-3}, acetone) 158 S cm^2 mol^{-1}.

[$AuCl_3$(Hepi)] 3. *Method (a).* An ethanol (5 cm^3) solution of 1-ethyl-2-phenylimidazole (0.522 g, 3.03 mmol) was added to a solution of $HAuCl_4$·$4H_2O$ (0.610 g, 1.48 mmol) in the same solvent (7.5 cm^3). The resulting mixture became a yellow suspension after stirring at room temperature for 1 h. After 1 d the yellow precipitates were collected and washed thoroughly with ethanol to give complex **3** (0.6667 g, 95%), mp 162 °C (Found: C, 27.85; H, 2.55; N, 5.85. $C_{11}H_{12}AuCl_4N_2$ requires C, 27.8; H, 2.55; N, 5.9%); ν $_{max}$/cm^{-1} (KBr) 367 (Au–Cl); Λ_M(1 × 10^{-3} mol dm^{-3}, acetone) 3.0 S cm^2 mol^{-1}.

Method (b). The salt **2** (0.051 g, 0.099 mmol) was stirred at room temperature in acetonitrile–water (1 : 5) for 3 d. The precipitated microcrystals were filtered off and washed thoroughly with ethanol to give complex **3** (0.0384 g, 81%).

[$AuCl_2$(epi-C^1,*N*)] 4. A dichloromethane (25 cm^3) solution of [$AuCl_3$(Hepi)] (0.341 g, 0.716 mmol) was added to a dichloromethane (25 cm^3) suspension of $AgBF_4$ (0.141 g, 0.724 mmol). The resulting mixture was refluxed for 6 h and then the volatile materials were removed *in vacuo*. The residue was extracted with acetonitrile to remove unreactive adduct **3**. The extract was evaporated to dryness and the residue extracted with dichloromethane. The dichloromethane extract was dried *in vacuo* and the resulting white residue washed successively with a small amount of acetonitrile and diethyl ether to give complex **4** (0.063 g, 20%), mp 270 °C (decomp.) (Found: C, 29.95; H, 2.55; N, 6.2. $C_{11}H_{11}AuCl_2N_2$ requires C, 30.1; H, 2.55; N, 6.4%); ν_{max}/cm^{-1} (KBr) 351 and 296 (Au–Cl).

[AuCl(epi-C^1,*N*)(PPh_3)]BF_4 5. To a suspension of [$AuCl_2$-(epi-C^1,*N*)] **4** (0.060 g, 0.138 mmol) in dichloromethane (5 cm^3) was added a solution of PPh_3 (0.038 g, 0.44 mmol) in dichloromethane (10 cm^3). After a few minutes $NaBF_4$ (0.077 g, 0.700 mmol) was added to the resulting pale yellow solution and the mixture stirred for 11 h at room temperature. Precipitated solids were removed by filtration and the filtrate was evaporated to dryness. The residue was extracted with ethanol and diluted with diethyl ether to give pale yellowish white microcrystals of complex **5** (0.061 g, 59%), mp 131 °C (Found: C, 46.15; H, 3.55;

N, 3.8. $C_{29}H_{26}AuBClF_4N_2P$ requires C, 46.25; H, 3.5; N, 3.7%); ν_{max}/cm^{-1} (KBr) 1055 (BF_4) and 315 (Au–Cl); $\Lambda_M(1 \times 10^{-3}$ M, acetone) 138 S cm² mol^{-1}.

[AuCl(epi-*C*^{1},*N*)(PPh$_3$)]PF$_6$ 6. This complex was similarly prepared as described for **5** using NH_4PF_6. Yield 56%, mp 200 °C (Found: C, 43.1; H, 3.3; N, 3.45. $C_{29}H_{26}AuClF_6N_2P_2$ requires C, 42.95; H, 3.25; N, 3.45%); ν_{max}/cm^{-1} (KBr) 834 (PF_6) and 311 (Au–Cl); $\Lambda_M(1 \times 10^{-3}$ M, acetone) 141 S cm² mol^{-1}.

X-Ray crystallography

Suitable crystals of [AuCl(epi-*C*^{1},*N*)(PPh$_3$)]PF$_6$ **6** were grown from dichloromethane–diethyl ether.

Crystal data. $C_{29}H_{26}AuClF_6N_2P_2$, $M = 810.90$, monoclinic, space group Cc, $a = 27.831(1)$, $b = 9.6282(3)$, $c = 23.3900(7)$ Å, $\beta = 115.012(1)°$, $U = 5679.9(3)$ Å^3, $D_c = 1.896$ g cm^{-3}, $Z = 8$, μ(Mo-Kα) = 54.68 cm^{-1}, $\lambda = 0.71069$ Å.

A yellow prismatic crystal having approximate dimensions of 0.10 × 0.25 × 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at −180 ± 1 °C and processed by the PROCESS-AUTO program package.[27] Of the 27031 reflections 6507 were unique ($R_{int} = 0.043$). An asymmetry-related absorption correction using the program ABSCOR[28] was applied. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods[29] and expanded using Fourier techniques.[30] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 6051 observed reflections ($I > 3.00\sigma(I)$) and 740 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.019$ and $R' = 0.017$.

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References

1 J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327; M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73; I. Omae, *Chem. Rev.*, 1979, **79**, 287; *Coord. Chem. Rev.*, 1980, **32**, 235; M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
2 R. V. Parish, *Gold Bull.*, 1997, **30**, 3.
3 E. C. Constable and T. A. Leese, *J. Organomet. Chem.*, 1989, **363**, 419.
4 C. W. Chan, W. T. Wong and C. M. Che, *Inorg. Chem.*, 1994, **33**, 1266.
5 H. O. Liu, T. C. Cheung, S. M. Peng and C. M. Che, *J. Chem. Soc., Chem. Commun.*, 1995, 1787.
6 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1995, 2865.
7 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1996, 4217.
8 Y. Fuchita, H. Ieda, Y. Tsunemune, J. Kinoshita-Kawashima and H. Kawano, *J. Chem. Soc., Dalton Trans.*, 1998, 791.
9 M. Nonoyama and K. Nakajima, *Polyhedron*, 1997, **16**, 4039.
10 Y. Fuchita, H. Ieda, A. Kayama, J. Kinoshita-Kawashima, H. Kawano, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1998, 4095.
11 J. Vicente, M. T. Chicote, M. I. Lozano and S. Huertas, *Organometallics*, 1999, **18**, 753.
12 M. Nonoyama, *Synth. React. Inorg. Metal-Org. Chem.*, 1999, **29**, 119.
13 Y. Fuchita, H. Ieda, S. Wada, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1999, 4431.
14 J. Vicente, M. T. Chicote and M. D. Bermudez, *Inorg. Chim. Acta*, 1982, **63**, 35; J. Vicente, M. T. Chicote, M. D. Bermudez, X. Solans and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1984, 557; J. Vicente, M. T. Chicote, M. D. Bermudez and M. Garcia-Garcia, *J. Organomet. Chem.*, 1985, **295**, 125.
15 J. Vicente, M. T. Chicote, M. D. Bermudez, M. J. Sanchez-Santano and P. G. Jones, *J. Organomet. Chem.*, 1986, **310**, 401.
16 J. Vicente, M. T. Chicote and M. D. Bermudez, *J. Organomet. Chem.*, 1984, **268**, 191; J. Vicente, M. T. Chicote, M. D. Bermudez, M. J. Sanchez-Santano and P. G. Jones, *J. Organomet. Chem.*, 1988, **354**, 381; J. Vicente, M. D. Bermudez, M. T. Chicote and M. J. Sanchez-Santano, *J. Organomet. Chem.*, 1989, **371**, 129; J. Vicente, M. D. Bermudez, M. J. Santano-Sanchez and J. Paya, *Inorg. Chim. Acta*, 1990, **174**, 53.
17 P. A. Bonnardel, R. V. Parish and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 3185.
18 J. Vicente, M. D. Bermudez, F. J. Carrion and P. G. Jones, *Chem. Ber.*, 1996, **129**, 1301.
19 M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson and A. D. C. Towl, *J. Am. Chem. Soc.*, 1971, **93**, 4591.
20 G. Minghetti, M. A. Cinellu, M. V. Pinna, S. Stoccoro, A. Zucca and M. Manessero, *J. Organomet. Chem.*, 1998, **568**, 225.
21 E. C. Constable, R. P. G. Henney, P. R. Raithby and L. R. Sousa, *J. Chem. Soc., Dalton Trans.*, 1992, 2251.
22 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
23 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.
24 J. Vicente, M. D. Bermudez, M. P. Carrillo and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1975.
25 J. Vicente, M. T. Chicote, M. D. Bermudez, P. G. Jones and G. M. Sheldrick, *J. Chem. Res.*, 1985, (*S*) 72; (*M*) 954.
26 H. J. J. Loozen, J. J. M. Drouen and O. Piepers, *J. Org. Chem.*, 1975, **40**, 3279.
27 PROCESS-AUTO, Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer, Rigaku Corporation, Tokyo, 1998.
28 T. Higashi, ABSCOR, Program for Absorption Correlation, Rigaku Corporation, Tokyo, 1995.
29 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
30 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. De Gelder, R. Israel and J. M. M. Smits, The DIRDIF 94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1994.

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