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N,*N*′,*N*″-Triphenylguanidinate(−1) complexes of ruthenium, osmium and iridium: synthesis and X-ray crystal structures[☆]

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Abstract

N,*N*′,*N*″-Triphenylguanidine (TpgH) reacts with $[Ru(H)_2(CO)(PPh_3)_3]$ in refluxing toluene and with $[Os(H)_2(CO)(PPh_3)_3]$ in refluxing *o*-xylene to yield the guanidinate(−1) complexes $[RuH(Tpg)(CO)(PPh_3)_2]$ (**1**) and $[Os(Tpg)_2(CO)(PPh_3)]$ (**2**), respectively. The reaction of TpgH with $[RuCl_2(PPh_3)_3]$ in refluxing toluene affords a new route to the known complex $[Ru(Tpg)_2(CO)(PPh_3)]$ (**3**). Finally the reaction of *mer*-$[Ir(H)_3(PPh_3)_3]$ with TpgH in refluxing toluene yields the iridium(III) dihydride complex $[Ir(H)_2(Tpg)(PPh_3)_2]$ (**4**). X-ray crystal structure determinations are reported for (**1**) and (**4**). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Guanidinato complexes; Ruthenium complexes; Osmium complexes; Iridium complexes; Crystal structures

1. Introduction

Transition metal complexes containing mono- or dianionic guanidinate ligands, though first reported many years ago [2,3], have only recently begun to attract significant attention. A small but rapidly growing number of such complexes containing chelate and/or bridging guanidinate(−1) ligands are now known [1,2,4–13] including several synthesised in our laboratory [1,4]. In addition complexes containing guanidinate(−2) ligands have been reported for iron [3], platinum [14] and, most recently niobium and tantalum [12]. In continuation of our previous work [1,4] in this active field we now report the synthesis of new *N*,*N*′,*N*″-triphenylguanidinate(−1) complexes of ruthenium, osmium and iridium by a direct route from metal hydride precursors and free guanidines. We also describe a new route to the previously reported [1] complex $[Ru(Tpg)_2(CO)(PPh_3)]$. X-ray crystal structures are presented for two of the new complexes, $[RuH(Tpg)(CO)(PPh_3)_2]$ (**1**) and $[Ir(H)_2(Tpg)(PPh_3)_2]$ (**4**)

2. Experimental

2.1. General procedures

N,*N*′,*N*″-Triphenylguanidine was obtained from Avocado Research Chemicals, the platinum metal precursors $[Ru(H)_2(CO)(PPh_3)_3]$, $[Os(H)_2(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ and *mer*-$[Ir(H)_3(PPh_3)_3]$ were prepared by literature methods [15]. Other reagents, experimental techniques and instrumentation were as described in a previous paper [16]. Infrared and NMR spectroscopic data are presented in Table 1.

2.2. $[Ru(H)\{PhNC(NHPh)NPh\}(CO)(PPh_3)_2]$ (1)

Carbonyldihydridotris(triphenylphosphine)ruthenium (0.6 g, 0.65 mmol) and *N*,*N*′,*N*″-triphenylguanidine (0.90 g, 3.14 mmol) were heated together under reflux in toluene (40 cm^3) for 8 h to give a dark green solution. Concentration under reduced pressure left an oil which on crystallisation from CH_2Cl_2–MeOH afforded pale yellow crystals (0.48 g, 79%), m.p. 196–198°C (Found: C, 70.85; H, 4.95; N, 4.35. *Anal.* Calc. for $C_{56}H_{47}N_3OP_2Ru$: C, 71.45; H, 5.05; N, 4.45%).

[☆] Complexes of the platinum metals. Part 51 [1].

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Table 1
Infrared [a] and NMR [b] spectroscopic data

Complex	ν(N–H)	ν(M–H)	ν(C=O)	δ(MH)	$^2J_{HP}$	δ(PPh$_3$)
[RuH(Tpg)(CO)(PPh$_3$)$_2$] (**1**)	3391	1971	1909	−13.20(t)	21	46.43(s)
[Os(Tpg)$_2$(CO)(PPh$_3$)] (**2**)			1894			10.22 (s)
[Ru(Tpg)$_2$(CO)(PPh$_3$)] (**3**)	3389		1918			52.59 (s)
	3400		1930			
[Ir(H)$_2$(Tpg)(PPh$_3$)$_2$] (**4**)	3377	2190		−22.84(t)	17.6	20.25 (s)
		2157				

[a] Nujol mulls/cm^{-1}.

[b] CDCl$_3$ solutions, J in Hz, s = singlet, t = triplet.

*2.3. [Os{PhNC(NHPh)NPh}$_2$(CO)(PPh$_3$)] (**2**)*

Carbonyldihydridotris(triphenylphosphine)osmium (0.40 g, 0.39 mmol) and N,N',N''-triphenylguanidine (0.68 g, 2.37 mmol) were heated together under reflux in o-xylene (40 cm^3) for 24 h to give a yellow–brown solution. Evaporation under reduced pressure left an oil which was crystallised from CH$_2$Cl$_2$–MeOH as lime-yellow crystals (0.23 g, 56%) (Found: C, 63.75; H, 4.3; N, 7.1. *Anal.* Calc. for C$_{57}$H$_{47}$N$_6$POOs C, 65.0; H, 4.5; N, 7.95%).

*2.4. [Ru{PhNC(NHPh)NPh}$_2$(CO)(PPh$_3$)] (**3**)*

Dichlorotris(triphenylphosphine)ruthenium (0.6 g, 0.63 mmol) and N,N',N''-triphenylguanidine (0.92 g, 3.2 mmol) were heated together under reflux in toluene (40 cm^3) for approximately 4.5 h to give a dark green–brown solution. Concentration under reduced pressure followed by crystallisation of the residue from CH$_2$Cl$_2$–MeOH afforded a few milligrams of an unidentified purple solid which was removed by filtration, followed by a main crop of lemon-yellow crystals (0.3 g, 50%) identical to an authentic sample prepared as previously described.

*2.5. [Ir(H)$_2${PhNC(NHPh)NPh}(PPh$_3$)$_2$] (**4**)*

mer-Trihydridotris(triphenylphosphine)iridium (0.4 g, 0.51 mmol) and N,N',N''-triphenylguanidine (0.74 g, 2.57 mmol) were heated together under reflux in toluene (40 cm^3) for approximately 18 h. to give a dark yellow–brown solution. Concentration under reduced pressure left an oil which on crystallisation from CH$_2$Cl$_2$–MeOH gave pale yellow crystals (0.28 g, 55%), m.p. 202–204°C (Found: C, 65.35; H, 4.6; N, 3.9. *Anal.* Calc. for C$_{55}$H$_{48}$N$_3$P$_2$Ir: C, 65.7; H, 4.8; N, 4.15%).

2.6. X-ray crystallography

Crystals were mounted on thin glass fibres using a fast setting epoxy resin, data were collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). For (**1**) a total of 360 oscillation frames of 60 s exposure time with 0.5° rotation in θ were recorded with a crystal detector distance of 35 mm, resulting in data complete to $2\theta = 42.5°$. The available software did not allow the collection of additional high-resolution data without extensive peak overlap. For (**4**) a total of 90 oscillation frames each of width 2° in θ and 30 s exposure time were recorded with a crystal detector distance of 25 mm. Crystals were indexed from the first ten frames using the DENZO package [17] and positional data were refined along with diffractometer constants to give the final cell parameters. Integration and scaling (DENZO Scalepack [17]) resulted in unique data sets corrected for Lorentz and polarisation effects, and for the effects of crystal decay and absorption, by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Crystallographic data are recorded in Table 2. The structures were solved using SHELXS-97 [18] and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97 [18]) with the aid of the programme RES2INS [19]. All non-hydrogen atoms were modelled anisotropically while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride except hydride ligands. In the case of (**1**) phenyl groups C(3)–C(8) and C(51)–C(56) exhibited elongated thermal ellipsoids, however attempts to model two alternate sets of positions for these rings were unsuccessful. A final difference Fourier maps for both compounds revealed the locations of the hydride ligands which were included in the model and their positional and thermal parameters refined freely. All calculations were carried out with either a Silicon graphics Indy R5000 work station or an IBM compatible PC.

3. Results and discussion

The reaction of [Ru(H)$_2$(CO)(PPh$_3$)$_3$] with N,N',N''-triphenylguanidine in refluxing toluene afforded the pale yellow air stable complex [RuH(Tpg)(CO)(PPh$_3$)$_2$]

Table 2
Crystallographic data for complexes **1** and **4**

Complex	**1**	**4**
Molecular formula	$C_{56}H_{47}N_3OP_2Ru$	$C_{55}H_{48}IrN_3P_2$
Molecular weight	940.98	1005.10
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*P*21/*a*
a (Å)	11.9120(2)	20.5315(2)
b (Å)	18.8830(3)	10.8110(2)
c (Å)	41.5780(7)	21.0185(4)
β (°)		105.725(1)
V (Å^3)	9352.3(3)	4490.78(13)
Z	8	4
Calculated density (g cm^{-3})	1.337	1.487
Absorption coefficient (mm^{-1})	0.447	3.086
F(000)	3888	2024
Crystal size (mm)	0.6 × 0.2 × 0.15	0.5 × 0.4 × 0.1
θ Range for data collection (°)	2.50 to 21.26	3.13 to 25.00
Index ranges		
h	0 to 12	0 to 22
k	0 to 19	0 to 12
l	0 to 42	−24 to 23
Reflections collected/unique	119,805/5038	31294/7600
R_{int}	0.032	0.0450
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5027/0/572	7600/0/563
Goodness-of-fit on F^2	1.307	1.081
Final *R* Indices [$I>2\sigma(I)$]	$R_1 = 0.0524$, $wR_2 = 0.1402$	$R_1 = 0.0298$, $wR_2 = 0.0741$
R indices (all data)	$R_1 = 0.0627$, $wR_2 = 0.2173$	$R_1 = 0.0345$, $wR_2 = 0.0777$
Largest difference peak and hole (e Å^{-3})	0.292 and −0.330	0.746 and −1.464

(**1**) in good yield. The infrared and NMR data are very similar to those previously recorded for the analogous amidinate complexes [RuH{PhNC(R)NPh}(CO)-$(PPh_3)_2$] [20] and established the *trans* phosphines stereochemistry. However, in order to learn more about the geometry of the chelated guanidinate ligand an X-ray crystal structure determination was undertaken. The molecular structure of (**1**) is shown in Fig. 1, selected bond length and angle data are collated in Table 3. The molecules are essentially octahedral with hydride, carbonyl, *trans* phosphines and chelate guanidinate(−1) ligands. However, the octahedral coordination sphere is distorted by the small bite angle [∠N–Ru–N = 59.6(2)°] of the guanidinate ligand. The ruthenium–nitrogen, -phosphorus and -carbon bond lengths are typical for octahedral ruthenium(II) and merit no further comment other than to note that the Ru–N bond *trans* to hydride [2.229(4) Å] is, as expected, significantly longer than that *trans* to carbonyl [2.164(5) Å]. The hydride ligand was located at a distance of 1.59 Å from the ruthenium. The planarity of the guanidinate ligand N_2CN skeleton is established by the sum of the angles subtended at the central carbon atom which equals 360.0°. As in previously reported *N*,*N*′,*N*″-triphenylguanidinate complexes of ruthenium(II) [1,7]

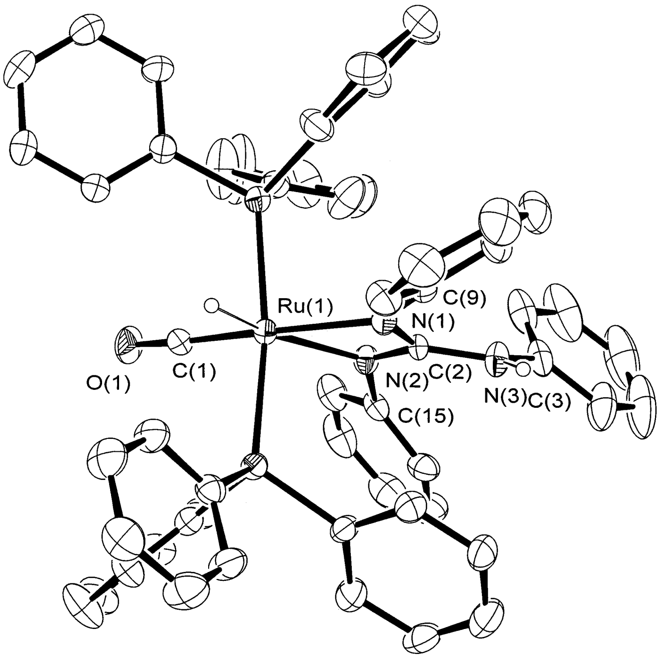

Fig. 1. Molecular structure of $[RuH(Tpg)(CO)(PPh_3)_2]$ (**1**) (ellipsoids drawn at 30% level, non-hydridic hydrogen atoms omitted for clarity).

Table 3
Selected bond lengths (Å) and angles and torsion angles (°) for $[RuH(Tpg)(CO)(PPh_3)_2]$ (**1**)

Ru–C(1)	1.818(6)	N(1)–C(2)	1.336(7)
Ru–N(1)	2.164(5)	N(1)–C(9)	1.403(7)
Ru–N(2)	2.229(4)	N(2)–C(2)	1.315(7)
Ru–P(2)	2.328(2)	N(2)–C(15)	1.413(8)
Ru–P(1)	2.384(2)	N(3)–C(2)	1.385(7)
O(1)–C(1)	1.168(7)	N(3)–C(3)	1.399(8)
		N(3)–H(N3)	0.86
C(1)–Ru–N(1)	167.2(2)	C(9)–N(1)–Ru	137.1(4)
C(1)–Ru–N(2)	108.0(2)	C(2)–N(2)–C(15)	126.0(5)
N(1)–Ru–N(2)	59.6(2)	C(2)–N(2)–Ru	93.4(3)
C(1)–Ru–P(2)	86.1(2)	C(15)–N(2)–Ru	134.4(4)
N(1)–Ru–P(2)	92.45(13)	C(2)–N(3)–C(3)	128.1(5)
N(2)–Ru–P(2)	98.26(13)	C(2)–N(3)–H(N3)	116
C(1)–Ru–P(1)	90.9(2)	C(3)–N(3)–H(N3)	116
N(1)–Ru–P(1)	92.54(13)	O(1)–C(1)–Ru	175.8(5)
N(2)–Ru–P(1)	91.74(13)	N(2)–C(2)–N(1)	111.0(5)
P(2)–Ru–P(1)	170.00(5)	N(2)–C(2)–N(3)	126.7(5)
C(2)–N(1)–C(9)	126.9(5)	N(1)–C(2)–N(3)	122.3(5)
C(2)–N(1)–Ru	95.8(3)		
N(1)–Ru–N(2)–C(2)	2.5(3)		

the dihedral angle between the N_2CN plane and the N–Ru–N plane is small [2.5(3)°] indicating very little folding of the chelate ring. The stereochemistry about the non-coordinated nitrogen N(3) is more uncertain. The attached hydrogen atom has been located but the associated errors are such that only one angle subtended at N(3) can be determined with precision [$\angle$C(2)–N(3)–C(3) = 128.1(5)°]. However, values of 116.0° obtained for each of the other two give a total of 360.1° and strongly support sp^2 trigonal planar hybridisation at N(3). The C–N bond lengths within the guanidinate chelate ring [1.336(7) and 1.315(7) Å] are consistent with a delocalised system involving substantial double bond character. However, the bond from the central carbon to the non-coordinated nitrogen, N(3), is considerably longer [1.385(7) Å] suggesting that there is relatively little delocalisation of the lone pair on N(3) over the N_2CN skeleton. Finally, the lengths of the N–C(Ph) bonds [av. 1.405(7) Å] indicate that there is little delocalisation of nitrogen lone-pair electron density out onto the attached phenyl rings. This conclusion is supported by the observation that the phenyl rings are rotated out of the N_2CN plane by approximately 30°.

The reaction of $[RuCl_2(PPh_3)_3]$ with *N*,*N*′,*N*″-triphenylguanidine in refluxing toluene afforded an alternative route to the known complex $[Ru(Tpg)_2(CO)(PPh_3)]$ (**3**) in fair yield. Characterisation of **3** was achieved by comparison with an authentic sample prepared by the original method [1]. The presence of a carbonyl ligand in the final product of the reaction is unexpected since no obvious source of CO is to hand. However, it is interesting to note that in an earlier study we observed that the reaction of $[RuCl_2(PPh_3)_3]$ with various amidines in refluxing toluene also gave fair yields of carbonyl containing products [20]. It appears that $[RuCl_2(PPh_3)_3]$ and certain related ruthenium(II) complexes in the presence of amidines and guanidines, have a particularly high affinity for carbonyl ligands. As in the case of the amidine reactions it appears probable that traces of alcohol or similar CO sources present in the toluene are responsible for the carbonylation.

Abstraction of hydride and carbonyl ligands from alcohols in the presence of base is a long established feature of ruthenium chemistry [21,22]. Therefore, given that amidines and, in particular, guanidines are strong organic bases a reaction of this nature seems entirely feasible in the present instance.

The reaction of $[Os(H)_2(CO)(PPh_3)_3]$ with *N*,*N*′,*N*″-triphenylguanidine in refluxing toluene did not give a clean product. However, a similar reaction in refluxing *o*-xylene afforded the bis(guanidinate) complex $[Os(Tpg)_2(CO)(PPh_3)]$ (**2**) in fair yield as air stable lime yellow crystals. Apart from the expected small shift in the ν(CO) frequency, the infrared spectra of the osmium complex **2** and its ruthenium analogue **3** are essentially identical. It is probable that complex **2** has the same *cis* CO–PPh_3 stereochemistry as complex **3**, and the available spectroscopic evidence (Table 1) appears consistent with this view. The bis(guanidinate) complex isolated from the present reaction contrasts with the hydrido(guanidinate) complex obtained from the same osmium precursor and *N*,*N*′-diphenylguanidine [4]. However, the difference can be attributed

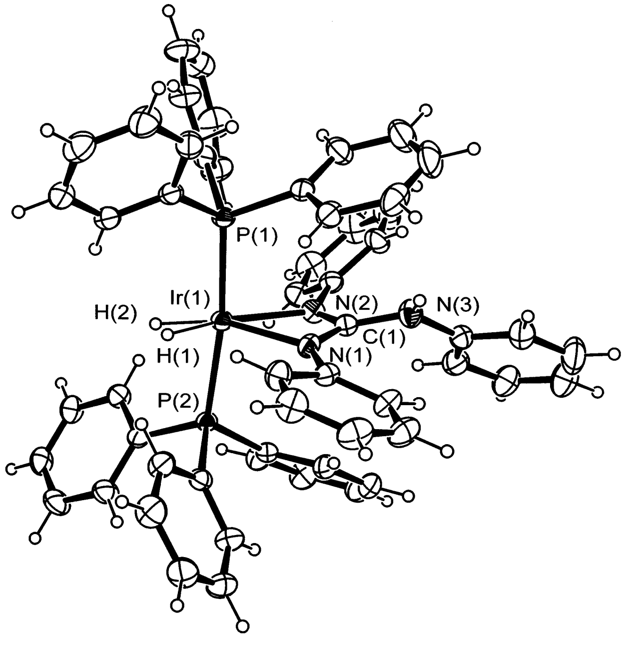

Fig. 2. Molecular structure of $[Ir(H)_2(Tpg)(PPh_3)_2]$ (**4**) (ellipsoids drawn at 30% level not omitted).

to the use of a lower boiling solvent (toluene) in the latter case.

The reaction of *mer*-[Ir(H)$_3$(PPh$_3$)$_3$] with *N*,*N*′,*N*″-triphenylguanidine in refluxing toluene affords the iridium(III) dihydride complex [Ir(H)$_2$(Tpg)(PPh$_3$)$_2$] (**4**) in good yield as air stable, pale yellow crystals. Spectroscopic data establish the *trans*-phosphines stereochemistry previously reported for the corresponding amidinate complexes [Ir(H)$_2${PhNC(R)NPh}(PPh$_3$)$_2$] [20]. However, as in the case of the ruthenium complex **1** an X-ray crystal structure analysis was undertaken to investigate the detailed geometry of the coordinated guanidinate ligand. The molecular structure of complex **4** is shown in Fig. 2, selected bond length and angle data are collated in Table 4. The complex is essentially octahedral, albeit highly distorted by the presence of a small ‘bite’ guanidinate ligand [$\angle$N–Ir–N = 59.49(12)°]. The iridium–phosphorus and –nitrogen bond lengths are within the ranges expected for octahedral iridium(III), with the latter reflecting the strong *trans* influence of the hydride ligands. The *cis* pair of hydride ligands have been located. The sum of the angles subtended at the central carbon atom of the guanidinate ligand [359.5°] establishes that, as in complex **1** and other previously reported guanidinate complexes [1,7] the N$_2$CN skeleton is rigorously planar. However, the dihedral angle between the N$_2$CN plane and the N–Ir–N plane [6.1(2)°] indicates folding of the chelate ring similar in magnitude to that reported for the rhodium(III) complex [RhCl(Tpg)(η-C$_5$Me$_5$)] [7] but larger than that found for *N*,*N*′,*N*″-triphenylguanidinate ligands chelated to ruthenium(II) [1,7] or palladium(II) [1]. Although the hydrogen atom attached to N(3) has been located the associated errors are such that only one angle subtended at N(3) can be measured accurately [$\angle$C(1)–N(3)–C(2) = 129.0(4)°]. However, values of 111.6 and 115.3° found for the other two give a total of 355.9°, which though someway short of the ideal (360°) suggests essentially sp^2 hybridisation about N(3). Bond length data for the guanidinate ligand point to delocalisation with significant C–N double bond character within the chelate ring [C–N 1.327(5) and 1.330(5) Å] but suggest that there is little delocalisation of the N(3) lone pair over the N$_2$CN skeleton [C(1)–N(3) 1.405(5) Å]. Likewise the lengths of the N–C(Ph) bonds [av. 1.399(5) Å] indicate that delocalisation of nitrogen lone pairs out onto the phenyl rings is minimal. This conclusion is supported by the observation that the phenyl rings are rotated out of the N$_2$CN skeletal plane by approximately 19–26°.

The presence of a hydrogen atom on the *exo*-cyclic (non-coordinated) nitrogen atoms in complexes **1** and **4** prevented the precise measurement of angles subtended at these centres. Consequently our conclusions concerning the geometry and electron distribution about these *exo*-cyclic nitrogens are of necessity rather tenuous. However recently reported X-ray crystal structure data for [Ta{CyNC(NMe$_2$)NCy}(NMe$_2$)$_4$] [23] do appear to offer support for our findings. In the tantalum complex the presence of two methyl groups on the *exo*-cyclic nitrogen atom of each guanidinate ligand permits accurate measurement of the angles subtended at this atom. These total 351.0 and 352.3° indicating essentially planar coordination in each case. Moreover the NMe$_2$ groups are twisted out of the guanidinate N$_2$CN skeletal plane by an average of 80.7° and the N$_2$C–NMe$_2$ distances (av. 1.42 Å) correspond to C–N single bonds. Taken together these results clearly indicate that while the *exo*-cyclic nitrogens are essentially sp^2 hybridised, their lone pair electron density is not significantly delocalised over the guanidinate skeleton. These conclusions are essentially similar to those reached for complexes **1** and **4** in the present work.

Table 4
Selected bond lengths (Å) and angles and torsion angles (°) for [Ir(H)$_2$(Tpg)(PPh$_3$)$_2$] (**4**)

Ir–N(1)	2.196(3)	N(2)–C(1)	1.330(5)
Ir–N(2)	2.217(3)	N(2)–C(14)	1.395(5)
Ir–P(2)	2.2862(9)	N(3)–C(2)	1.396(5)
Ir–P(1)	2.3062(10)	N(3)–C(1)	1.405(5)
N(1)–C(1)	1.327(5)	N(3)–H(N3)	0.926
N(1)–C(8)	1.407(5)		
N(1)–Ir–N(2)	59.49(12)	C(1)–N(2)–C(14)	129.6(3)
N(1)–Ir–P(2)	91.64(9)	C(1)–N(2)–Ir	93.7(2)
N(2)–Ir–P(2)	96.27(9)	C(14)–N(2)–Ir	133.1(3)
N(1)–Ir–P(1)	92.61(9)	C(2)–N(3)–C(1)	129.0(4)
N(2)–Ir–P(1)	91.85(9)	C(2)–N(3)–H(N3)	115.3
P(2)–Ir–P(1)	171.88(4)	C(1)–N(3)–H(N3)	111.6
C(1)–N(1)–C(8)	128.5(3)	N(1)–C(1)–N(2)	111.0(3)
C(1)–N(1)–Ir	94.8(2)	N(1)–C(1)–N(3)	121.2(4)
C(8)–N(1)–Ir	136.8(3)	N(2)–C(1)–N(3)	127.3(4)
N(2)–Ir–N(1)–C(1)	6.1(2)		

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary material publication nos. CCDC 141389 and 141390. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.uk).

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References

[1] Part 50. K.T. Holman, S.D. Robinson, A. Sahajpal, J.W. Steed, J. Chem. Soc., Dalton Trans. (1999) 15.

[2] G. Chandra, A.D. Jenkins, M.F. Lappert, R.C.Srivastava, J. Chem. Soc. A (1970) 2250.

[3] N.J. Bremer, A.B. Cutcliffe, M.F. Farona, W.G. Kofron, J. Chem. Soc. A (1971) 3264; N.J. Bremer, A.B. Cutcliffe, M.F. Farona, Chem. Commun. (1970) 932.

[4] S.D. Robinson, A. Sahajpal, J. Chem. Soc., Dalton Trans. (1997) 3349.

[5] P.J. Bailey, S.F. Bone, L.A. Mitchell, S. Parsons, K.J. Taylor, L.J. Yellowlees, Inorg. Chem. 36 (1997) 867.

[6] J.R. Da, S. Maia, P.A. Gazard, M. Kilner, A.S. Batsanov, J.A.K. Howard, J. Chem. Soc., Dalton Trans. (1997) 4625.

[7] P.J. Bailey, L.A. Mitchell, S. Parsons, J. Chem. Soc., Dalton Trans. (1996) 2839.

[8] H.-K. Yip, C.-M. Che, Z.-Y. Zhou, T.C.W. Mak, J. Chem. Soc., Chem. Commun. (1992) 1369.

[9] E.M.A. Ratillo, B.K. Scott, M.S. Moxness, N.M. Kostic, Inorg. Chem. 29 (1990) 918.

[10] P.J. Bailey, A.J. Blake, M. Kryszczuk, S. Parsons, D. Reed, J. Chem. Soc., Chem. Commun. (1995) 1647.

[11] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 38 (1999) 998 and 6728.

[12] M.K.T. Tin, N. Thirupathi, G.P.A. Yap, D.S. Richeson, J. Chem. Soc., Dalton Trans. (1999) 2947.

[13] J.M. Decams, L.G. Hubert-Pfalzgraf, J. Vaissermann, Polyhedron 18 (1999) 2885.

[14] M.B. Dinger, W. Henderson, Chem. Commun. (1996) 221.

[15] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.

[16] S.D. Robinson, A. Sahajpal, D.A. Tocher, J. Chem. Soc., Dalton Trans. (1995) 3497.

[17] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), Methods in Enzymology, Academic Press, New York, 1996, p. 276.

[18] G.M. Sheldrick, SHELXS-97 and SHELXL-97, programs for the solution and refinement of X-ray crystal structures, University of Göttingen, 1997.

[19] L.J. Barbour, RES2INS, a graphical interface for the interpretation and refinement of crystallographic data, University of Missouri-Columbia, 1995.

[20] T. Clark, S.D. Robinson, J. Chem. Soc., Dalton Trans. (1993) 2827.

[21] J. Chatt, B.L. Shaw, A.E. Field, J. Chem. Soc. (1964) 3466; Chem. Ind. (London) (1960) 931.

[22] L. Vaska, J.W. Di Luzio, J. Am. Chem. Soc. 83 (1961) 1262.

[23] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 38 (1999) 998.