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Synthesis and structure of an *ortho*-metallated ketazine complex of osmium, $\overline{\text{OsH(CO)}_2[(\text{C}_6\text{H}_3\text{-}p\text{-Me})(p\text{-tolyl})\text{CN}}\text{NC}(p\text{-tolyl})_2](\text{PPh}_3)$

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Abstract

Reaction of $Os(CO)_2(PPh_3)_2$ with a two-fold excess of di-*p*-tolyldiazomethane in benzene at reflux temperature affords the yellow $\overline{\text{OsH(CO)}_2[(\text{C}_6\text{H}_3\text{-}p\text{-Me})(p\text{-tolyl})\text{CN}}\text{NC}(p\text{-tolyl})_2](\text{PPh}_3)$ (A) in high yield. The structure of A has been determined by X-ray crystallography. The geometry about osmium is octahedral, with the hydride ligand *trans* to triphenylphosphine and the carbonyl ligands mutually *cis*. The ketazine ligand is bound to osmium through nitrogen and the *ortho*-carbon of a *p*-tolyl group. The Os–N and Os–C distances are 2.119(5) and 2.100(7) Å, respectively.

Introduction

The osmium complex $OsCl(NO)(PPh_3)_3$ undergoes reaction at room temperature with the diazoalkanes CH_2N_2[1], CH_3CHN_2, *p*-tolylCHN_2, and EtO_2CCHN_2 [2], to afford the corresponding mononuclear alkylidene complexes $Os(=CHR)Cl(NO)(PPh_3)_2$ in 80–90% yield. To determine whether the diazoalkane reaction offers a route to di-substituted alkylidene complexes, in addition to methylene and mono-substituted alkylidene complex formation, the reactions of $OsCl(NO)(PPh_3)_3$ with di-*p*-tolyldiazomethane and diphenyldiazomethane were investigated. $OsCl(NO)(PPh_3)_3$ was recovered unchanged, even after prolonged boiling in benzene with an excess of the diazo compound. Surprisingly, however, the related zerovalent osmium compound $Os(CO)_2(PPh_3)_3$ does react with two equivalents of $(p\text{-tolyl})_2CN_2$ at 80 ° C to give a yellow crystalline product. This is not an alkylidene complex but an *ortho*-metallated ketazine complex, the characterisation of which is reported in this paper.

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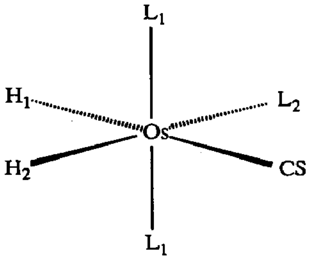
Results and discussion

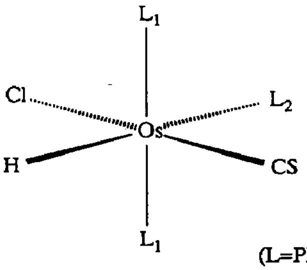
Spectroscopic characterisation

The ^1H NMR spectrum of this product shows four singlet resonances of equal intensity in the range δ 2.15–2.40, corresponding to the methyl signals of four chemically inequivalent *p*-tolyl groups. The resonances for the aryl protons of these groups are superimposed on those for the triphenylphosphine protons, forming a multiplet at δ 6.6–7.5. The integral for this multiplet and the collective integral for the four methyl signals are in the approximate ratio 5 : 2, suggesting the presence of only one triphenylphosphine ligand in this complex.

A doublet at δ −6.05 ($^2J(PH) = 72$ Hz) indicates the presence of an osmium-bound hydride ligand coupling to one phosphorus atom only. The magnitude of $^2J(PH)$ suggests that the hydride and triphenylphosphine ligands are mutually *trans* (cf. coupling constants for the osmium thiocarbonyl–phosphine–hydride complexes below [3]).



$^2J(P_1H_2)$=28.0Hz
$^2J(P_2H_2)$=60.5Hz

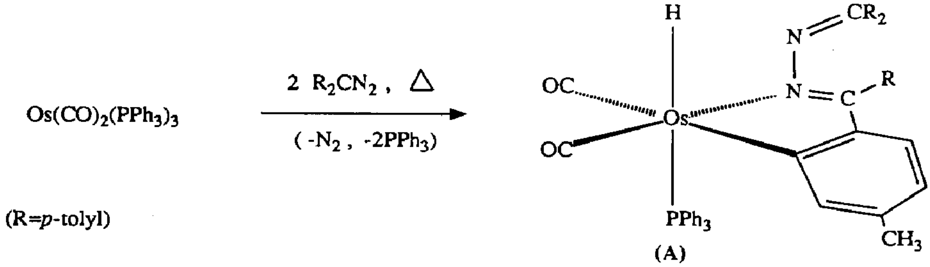


$^2J(P_1H)$=24.5Hz
$^2J(P_2H)$=93.0Hz

(L=PPh_3)

The IR spectrum of this compound shows ν(CO) bands at 1993 and 1927 cm^{-1} and the ν(Os–H) band is seen as a shoulder at 2018 cm^{-1}. There is much IR activity in the range 1600–780 cm^{-1} and specific assignment of many of these bands is not possible. Activity at 1610 cm^{-1} could be associated with C=N stretching, with azines and hydrazones typically absorbing in the range 1605–1630 cm^{-1}.

The ^1H NMR and IR spectroscopic data are thus consistent with a product that contains an *ortho*-metallated ketazine ligand i.e.:



(R=*p*-tolyl)

(A)

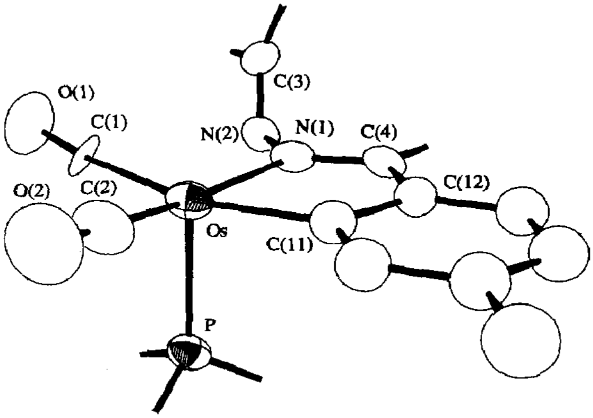


Fig. 1. Molecular geometry for $\overline{\mathrm{OsH(CO)_2[(C_6H_3\text{-}}p\mathrm{\text{-}Me)(}p\mathrm{\text{-}tolyl)CN}}\mathrm{NC(}p\mathrm{\text{-}tolyl)_2]PPh_3}$ with phenyl and tolyl rings omitted for clarity.

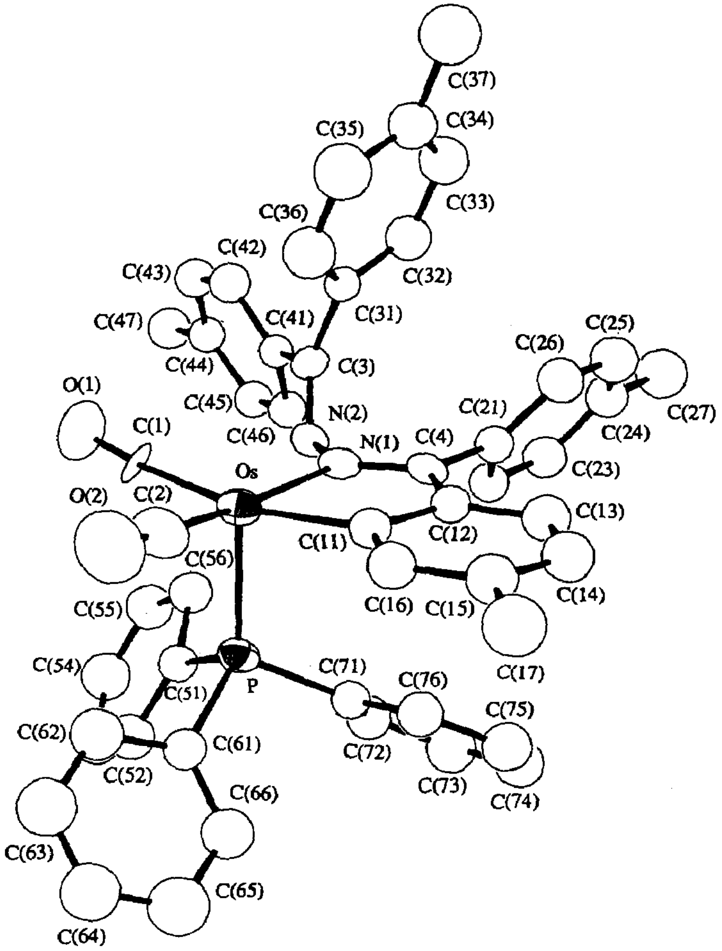


Fig. 2. Molecular geometry for $\overline{\mathrm{OsH(CO)_2[(C_6H_3\text{-}}p\mathrm{\text{-}Me)(}p\mathrm{\text{-}tolyl)CN}}\mathrm{NC(}p\mathrm{\text{-}tolyl)_2]PPh_3}$.

Table 1

Atomic coordinates for $\overline{\mathrm{OsH(CO)_2[(C_6H_3\text{-}\mathit{p}\text{-}Me)(\mathit{p}\text{-}tolyl)C}}\mathrm{NNC(\mathit{p}\text{-}tolyl)_2](PPh_3)}$ (A)

	x	y	z	B_{eq} (or B_{iso})
Os	0.10682(4)	0.29428(2)	0.10578(4)	3.3
P	0.2519(3)	0.3799(2)	0.2657(3)	3.4
C(1)	0.1369(10)	0.3071(5)	−0.0583(11)	4.3
O(1)	0.1516(9)	0.3089(4)	−0.1599(8)	7.3
C(2)	−0.0584(11)	0.3419(6)	0.0546(12)	5.0
O(2)	−0.1673(8)	0.3686(5)	0.0233(10)	7.7
N(1)	0.2703(7)	0.2233(4)	0.1657(7)	2.9
N(2)	0.3683(7)	0.2164(4)	0.1035(7)	3.2
C(3)	0.3699(9)	0.1673(5)	0.0140(9)	3.1
C(4)	0.2869(9)	0.1930(4)	0.2689(9)	3.2
C(11)	0.0812(9)	0.2575(5)	0.2669(9)	3.5(1)
C(12)	0.1792(9)	0.2102(5)	0.3278(9)	3.1(1)
C(13)	0.1828(10)	0.1831(5)	0.4424(11)	4.4(1)
C(14)	0.0773(11)	0.2019(6)	0.4947(11)	4.9(2)
C(15)	−0.0225(11)	0.2467(5)	0.4341(11)	4.8(2)
C(16)	−0.0260(9)	0.2753(5)	0.3233(10)	4.3(2)
C(17)	−0.1406(13)	0.2683(7)	0.4919(13)	6.6(2)
C(21)	0.4030(9)	0.1452(5)	0.3182(9)	3.4(1)
C(22)	0.5386(9)	0.1639(5)	0.3599(10)	3.8(2)
C(23)	0.6512(11)	0.1180(5)	0.4009(11)	4.5(2)
C(24)	0.6271(9)	0.0539(5)	0.4006(10)	4.3(2)
C(25)	0.4949(10)	0.0372(6)	0.3601(11)	5.2(2)
C(26)	0.3802(10)	0.0809(5)	0.3188(11)	4.6(2)
C(27)	0.7494(12)	0.0055(6)	0.4455(12)	6.5(2)
C(31)	0.2841(9)	0.1103(4)	−0.0329(9)	3.0(1)
C(32)	0.3467(10)	0.0502(5)	−0.0130(11)	4.8(2)
C(33)	0.2713(11)	−0.0064(6)	−0.0572(11	5.4(2)
C(34)	0.1325(11)	−0.0029(5)	−0.1215(11)	4.9(2)
C(35)	0.0645(12)	0.0578(6)	−0.1464(12)	6.9(3)
C(36)	0.1420(11)	0.1151(6)	−0.0986(12)	6.0(2)
C(37)	0.0464(12)	−0.0632(7)	−0.1735(13)	7.7(3)
C(41)	0.4763(9)	0.1675(4)	−0.0469(9)	3.0(1)
C(42)	0.4462(10)	0.1426(5)	−0.1874(10)	4.3(2)
C(43)	0.5417(10)	0.1472(5)	−0.2485(10)	4.3(2)
C(44)	0.6657(9)	0.1755(5)	−0.1690(10)	3.7(2)
C(45)	0.6972(10)	0.1988(5)	−0.0274(10)	3.9(2)
C(46)	0.6008(10)	0.1960(5)	0.0338(10)	3.8(2)
C(47)	0.7668(11)	0.1830(5)	−0.2399(11)	5.2(2)
C(51)	0.3717(9)	0.4097(5)	0.2087(9)	3.4(1)
C(52)	0.4027(10)	0.4764(5)	0.2404(11)	5.1(2)
C(53)	0.5078(12)	0.4952(6)	0.2025(12)	6.4(2)
C(54)	0.5775(12)	0.4520(6)	0.1368(12)	6.1(2)
C(55)	0.5479(11)	0.3863(6)	0.1042(12)	5.4(2)
C(56)	0.4429(10)	0.3648(5)	0.1395(11)	4.4(2)
C(61)	0.1569(9)	0.4547(5)	0.3064(10)	3.7(2)
C(62)	0.0526(10)	0.4784(6)	0.1940(11)	5.5(2)
C(63)	−0.0242(12)	0.5361(6)	0.2179(11)	6.7(3)
C(64)	0.0081(12)	0.5659(6)	0.3541(12)	6.7(3)
C(65)	0.1091(12	0.5441(7)	0.4637(12)	7.2(3)
C(66)	0.1906(10)	0.4843(6)	0.4427(11)	5.5(2)
C(71)	0.3656(9)	0.3597(5)	0.4396(9)	3.3(1)
C(72)	0.5110(10)	0.3617(5)	0.4874(11)	4.6(2)
C(73)	0.5942(11)	0.3438(6)	0.6232(12)	5.6(2)
C(74)	0.5349(11)	0.3272(6)	0.7066(12)	5.4(2)
C(75)	0.3932(11)	0.3240(6)	0.6575(12)	5.2(2)
C(76)	0.3064(10)	0.3408(5)	0.5248(10)	4.3(2)

Table 2

Interatomic distances for $\overline{\text{OsH(CO)}_2[(\text{C}_6\text{H}_3\text{-}p\text{-Me})(p\text{-tolyl})\text{CN}}\text{NC}(p\text{-tolyl})_2](\text{PPh}_3)$ (A)

Os–P	2.440(2)	C(2)–O(2)	1.168(9)
Os–C(1)	1.932(9)	N(1)–N(2)	1.406(7)
Os–C(2)	1.839(8)	N(1)–C(4)	1.296(8)
Os–N(1)	2.119(5)	N(2)–C(3)	1.270(8)
Os–C(11)	2.100(7)	C(3)–C(31)	1.485(9)
P–C(51)	1.809(7)	C(3)–C(41)	1.494(9)
P–C(61)	1.847(8)	C(4)–C(12)	1.476(10)
P–C(71)	1.833(7)	C(4)–C(21)	1.477(10)
C(1)–O(1)	1.141(9)		

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=7$
C(i1)–C(i2)	1.38(1)	1.40(1)	1.37(1)	1.39(1)	1.43(1)	1.38(1)	1.42(1)
C(i1)–C(i6)	1.46(1)	1.41(1)	1.38(1)	1.39(1)	1.41(1)	1.37(1)	1.41(1)
C(i2)–C(i3)	1.41(1)	1.42(1)	1.42(1)	1.41(1)	1.43(1)	1.42(1)	1.42(1)
C(i3)–C(i4)	1.41(1)	1.41(1)	1.35(1)	1.38(1	1.37(1)	1.37(1)	1.39(1)
C(i4)–C(i5)	1.36(1)	1.36(1)	1.41(1)	1.39(1)	1.41(1)	1.33(1)	1.38(1)
C(i5)–C(i6)	1.39(1)	1.40(1)	1.44(1)	1.41(1)	1.44(1)	1.48(1)	1.41(1)
C(i4)–C(i7)	1.58(1)	1.52(1)	1.54(1)	1.56(1)			

To confirm this postulate, an X-ray crystal structure determination was undertaken.

X-ray crystal structure

The molecular geometry of $\overline{\text{OsH(CO)}_2[(\text{C}_6\text{H}_3\text{-}p\text{-Me})(p\text{-tolyl})\text{C=N}}\text{–NC}(p\text{-tolyl})_2](\text{PPh}_3)$ (A) is shown in Figs. 1 and 2. Important bond distances and angles are presented in Tables 2 and 3.

The hydride ligand was not located. An apparently vacant coordination site *trans* to the phosphine ligand is evident, however, and the ^{1}NMR data confirm that this is the site occupied by the hydride ligand. The overall geometry is therefore octahedral, as would be expected for an osmium(II) complex.

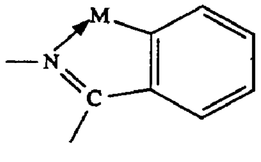
Table 3

Bond angles for $\overline{\text{OsH(CO)}_2[(\text{C}_6\text{H}_3\text{-}p\text{-Me})(p\text{-tolyl})\text{CN}}\text{NC}(p\text{-tolyl})_2](\text{PPh}_3)$ (A)

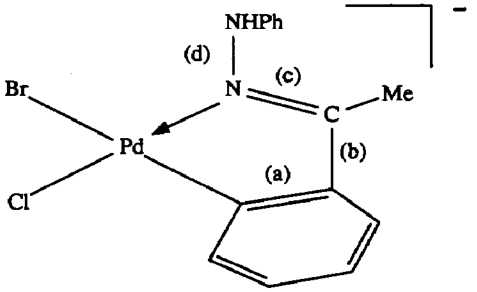
P–Os–C(1)	95.7(2)	Os–N(1)–C(4)	119.8(5)
P–Os–C(2)	97.5(2)	Os–N(1)–N(2)	118.3(4)
P–Os–N(1)	92.2(2)	C(4)–N(1)–N(2)	121.4(6)
P–Os–C(11)	94.2(2)	N(1)–N(2)–C(3)	120.0(5)
C(1)–Os–C(2)	92.6(4)	N(2)–C(3)–C(31)	128.6(6)
C(1)–Os–N(1)	94.7(3)	N(2)–C(3)–C(41)	114.1(6)
C(1)–Os–C(11)	166.3(3)	N(1)–C(4)–C(12)	113.6(6)
C(2)–Os–N(1)	167.2(3)	N(1)–C(4)–C(21)	121.6(6)
C(2)–Os–C(11)	95.4(3)	C(12)–C(4)–C(21)	124.8(6)
N(1)–Os–C(11)	75.5(2)	C(4)–C(12)–C(11)	115.0(6)
Os–P–C(51)	116.9(2)	Os–C(11)–C(12)	116.0(5)
Os–P–C(61)	114.9(2)	Os–C(1)–O(1)	173.7(8)
Os–P–C(71)	115.5(2)	Os–C(2)–O(2)	175.3(7)

The crystal structure confirms that complex A contains the *ortho*-metallated ketazine ligand, bis(*p*-tolyl)methylenebis(*p*-tolyl)methanone hydrazone. The Os–N(1) bond length of 2.119(5) Å and the Os–C(11) bond length of 2.100(7) Å are typical for Os–N and Os–C(aryl) single bonds respectively (cf. values of *d*(Os–N) = 2.120(6) Å and *d*(Os–C(aryl)) = 2.106(7) Å in $Os(CO)_2(C_6H_4NNC_6H_5)_2$ [4].

Although the generation of an *ortho*-metallated ketazine ligand system in a transition metal complex has been recognized as being perfectly feasible [5], the osmium compound appears to be the first such complex to be reported. This ketazine complex belongs to a class of compounds termed *ortho*-metallated benzylidene-amines [6], which are chelate complexes of the form:



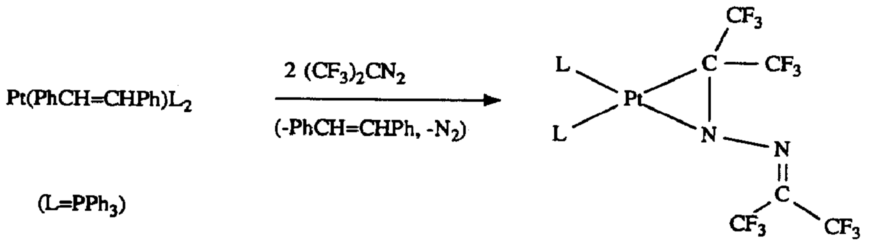
The structurally characterised complex $[^nBu_4N][Pd(C_6H_4C(Me){=}NNHPh)ClBr]$ contains a ligand of this type [7]:



and the bond lengths labelled (a)–(d) are very similar to the corresponding distances in the ketazine ligand of the osmium complex.

Other ketazine complexes

Other azine complexes have been reported from the room temperature reactions of bis(trifluoromethyl)diazomethane with several d^{10} metal complexes [8] e.g.:



This platinum complex has been structurally characterised, and the crystal structure confirms that the azine is η^2-bound to the metal via one of the carbon–nitrogen double bonds. This contrasts with the coordination of the *ortho*-metallated osmium complex, A, in which the ketazine nitrogen is σ-bound to the metal centre.

A possible mechanism for ketazine formation

Pyrolysis of (p-tolyl)$_2$CN$_2$ generates the ketazine, (p-tolyl)$_2$CNNC(p-tolyl)$_2$ [9]. It is plausible, then, that the formation of the osmium complex, A, could arise from coordination of the free azine generated in situ from the diazo compound. However, when Os(CO)$_2$(PPh$_3$)$_3$ is heated under reflux in benzene with the preformed azine (p-tolyl)$_2$CNNC(p-tolyl)$_2$, no OsH(CO)$_2$[(C$_6$H$_3$-p-Me)(p-tolyl)CNNC(p-tolyl)$_2$]-(PPh$_3$) is formed. This suggests that the *ortho*-metallated product is produced via an intermediate diazoalkane complex, with the ketazine ligand being formed within the coordination sphere of the metal. Proposals for the nature of the appropriate intermediate must remain speculative but some reasonable assumptions may be made. The formation of a mono-phosphine product from a *trans*-bis(triphenylphosphine)osmium(II) complex is most unusual, and suggests that very unfavourable steric interactions are being developed in an intermediate species. Such interactions could reasonably arise in this reaction if the Os(CO)$_2$(PPh$_3$)$_2$ fragment formed a π-bound adduct with (p-tolyl)$_2$CN$_2$, via the C=N bond of the diazoalkane. π-Acceptance into orbitals based on C and N would force the p-tolyl groups into the vertical plane containing the phosphine ligands, causing significant steric interactions.

Phosphine displacement from the η^2-C,N-intermediate, *ortho*-metallation, and then attack by a second molecule of (p-tolyl)$_2$CN$_2$ at the electron-rich *exo*-nitrogen could generate the observed final product, A.

Another possibility would involve the intermediacy of the tertiary alkylidene complex Os[=C(p-tolyl)$_2$](CO)$_2$(PPh$_3$)$_2$, but there is no evidence for this compound.

Experimental

The general procedures used have been described previously [10]. IR spectra were recorded on a Perkin Elmer 597 spectrometer with Nujol mulls between KBr plates. ^{1}H NMR spectra were recorded on a Varian T60 instrument. Os(CO)$_2$(PPh$_3$)$_3$ [11] and (p-tolyl)$_2$CN$_2$ [9] were prepared by published methods.

OsH(CO)$_2$[(C$_6$H$_3$-p-CH$_3$)(p-tolyl)CNNC(p-tolyl)$_2$](PPh$_3$)

A solution of Os(CO)$_2$(PPh$_3$)$_2$ (200 mg) and (p-tolyl)$_2$CN$_2$ (50 mg) in benzene (15 mL) was heated under reflux for 10 min. The resulting yellow solution was allowed to cool, methanol (20 mL) was added, and solvent removed under reduced pressure to afford yellow microcrystals of the product. A sample of analytical quality was obtained by chromatography on a 3 × 3 cm column of silica gel with CH$_2$Cl$_2$ as eluent. Recrystallisation from CH$_2$Cl$_2$/MeOH gave yellow crystals of the product (145 mg, 82%) m.p. 234–236 °C. Anal. Found: C,64.13; H,5.22; N, 2.91. C$_{50}$H$_{43}$N$_2$O$_2$OsP calcd.: C,64.92; H,4.69; N,3.03%.

IR Absorptions. (cm^{-1}) 2018sh (ν(Os–H)); 1993,1927(vs) (ν(CO)); 1610(w),1584(m) (ν(CN)); other bands at 1528,1501(w),1440,1189,1102(m),839(w), 823,804,799(m),781(w).

^{1}H NMR chemical shifts. (δ, measured in CDCl$_3$) −6.05 (d,1H,Os–H,^2J(PH) = 72 Hz); 2.15 (s,3H,CH_3); 2.23 (s,3H,CH_3); 2.28 (s,3H,CH_3); 2.40 (s,3H,CH_3); 6.6–7.5 (m,30H,aromatic H's).

X-ray crystallography

Crystals of $\overline{\mathrm{OsH(CO)_2[(C_6H_3\text{-}}p\mathrm{\text{-}CH_3)(}p\mathrm{\text{-}tolyl)CN}}\mathrm{NC(}p\mathrm{\text{-}tolyl)_2](PPh_3)}$ were obtained from $CH_2Cl_2/EtOH$. $C_{50}H_{43}N_2O_2OsP$, $M = 924.17$, triclinic, space group $P1$, a 10.554(2), b 21.144(4), c 10.452(1) Å, α 100.37(1), β 113.32(1) γ 83.24(1)°, U 2104.1 $Å^3$, $Z = 2$, $D_c = 1.549$ g cm^{-3},Mo-K_α radiation λ 0.71069Å, μ(Mo-K_α) = 34.9 cm^{-1}. Intensities of 4193 reflections [$3579 > 3\sigma(I)$] were measured on a Nonius CAD-4 diffractometer using the $\omega/2\theta$ scan technique and Zr-filtered Mo-K_α radiation. The intensities of three reflections were monitored through the data collection as a check for misalignment or decomposition, no evidence for either being found. Data were corrected for Lorentz and polarisation effects and empirical absorbtion corrections applied. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares (weight $= 1/(\sigma(F) + 0.001F^2)$, refinement converged to $R = 0.042$, $R_w = 0.050$. Hydrogen atoms were allowed to move, at a fixed distance of 1.08 Å from the carbon atom to which they are bound, and with fixed thermal parameters. Atomic coordinates are listed in Table 1 and bond distances and angles in Tables 2 and 3, respectively. Thermal parameters and tables of F_{obs} and F_{calc} are available from the authors.

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