Complexes of the Platinum Metals. Part 37.[1] Benzotriazole and 5,6-Dimethylbenzotriazole Derivatives. *X*-Ray Crystal Structure of Carbonylhydrido[hydrogenbis(benzotriazolato)]bis(triphenylphosphine)osmium(II)†

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The ruthenium and osmium complexes [MH(Cl)(CO)(PPh$_3$)$_3$] (M = Ru or Os) each react with benzotriazole (Hbta) in cold benzene to form a pair of geometrical isomers [MH(Cl)(Hbta)(CO)(PPh$_3$)$_2$] (H *trans* to Hbta or Cl). The dihydrides [MH$_2$(CO)(PPh$_3$)$_3$] react with excess of benzotriazole in boiling benzene (M = Ru) or toluene (M = Os) to afford products of the form [MH(bta ••• H–bta)(CO)(PPh$_3$)$_2$] containing a hydrogen-bonded benzotriazole–benzotriazolate pair co-ordinated as an NN′ chelate ligand. Similar chelate ligands are found in the products *trans*-[M(bta ••• H–bta)$_2$(Hbta)(PPh$_3$)] obtained from [RuH$_2$(PPh$_3$)$_4$] and Hbta in boiling benzene, or from [MCl$_2$(PPh$_3$)$_3$], Hbta, and triethylamine in boiling benzene (M = Ru) or toluene (M = Os). Isomeric forms of the complexes *trans*-[M(bta ••• H–bta)$_2$(Hbta)(PPh$_3$)] are thought to involve N^2- or N^3-co-ordinated Hbta ligands. Treatment of [IrCl(CO)(PPh$_3$)$_2$] with Hbta leads to reversible formation of the oxidative-addition product [IrH(Cl)(bta)(CO)(PPh$_3$)$_2$] in solution. The same reagents in the presence of NEt$_3$ afford the known complex [Ir(bta)(CO)(PPh$_3$)$_2$]. Benzotriazole also reacts with *mer*-[IrH$_3$(PPh$_3$)$_3$] to form [IrH$_2$(bta ••• H–bta)(PPh$_3$)$_2$] and with [Pt(PPh$_3$)$_4$] to generate [Pt(bta)$_2$(PPh$_3$)$_2$]. The nature of the hydrogen-bonded composite (bta ••• H–bta) ligand has been confirmed by an *X*-ray diffraction study on the osmium complex [OsH(bta ••• H–bta)(CO)(PPh$_3$)$_2$]. The crystals are triclinic, space group $P\bar{1}$, with a = 10.059(4), b = 11.876(1), c = 20.629(3) Å, α = 74.57(1), β = 83.08(2), γ = 65.96(2)°, and Z = 2. A parallel series of complexes have been obtained using 5,6-dimethylbenzotriazole.

The anti-corrosion properties of benzotriazole Hbta (**1**) (Scheme) towards transition metals, particularly copper,[2] have focused attention on the co-ordination chemistry of the parent molecule and its conjugate base, the benzotriazolate anion (bta$^-$). This attention has been rewarded by the synthesis of a wide variety of complexes in which the benzotriazolate anion is co-ordinated in monodentate (N^1 or N^2), bridging bidentate (N^{1}N^2 or N^{1}N^3), or bridging tridentate (N^{1}N^{2}N^3) bonding modes.[2] However, by virtue of their cyclic structure neither benzotriazole nor the benzotriazolate anion can function as a simple chelate ligand.

We have now found that a combination of the two in the form of the hydrogen-bonded composite ligand (**2**) is able to bond in chelate fashion to form a range of stable complexes, and we have used *X*-ray diffraction methods to characterise one of these products and confirm the nature of the chelate bta ••• H–bta. We have also synthesised new N^1-bonded benzotriazolate derivatives and isomeric pairs of complexes containing N^2- and N^3-co-ordinated benzotriazole ligands.

The physical and chemical properties of benzotriazole, its co-ordination chemistry, and its use as an analytical agent for platinum-group metals have been discussed in a monograph[3] and a recent review.[2] A preliminary report on some of the work contained in this paper has appeared elsewhere.[4]

Experimental

For general experimental details, see Part 29.[5] Benzotriazole and 5,6-dimethylbenzotriazole hydrate were obtained from Aldrich and used without further purification. Platinum metal starting materials were prepared using published methods.[6]

Syntheses.—[RuH(bta ••• H–bta)(CO)(PPh$_3$)$_2$]. A mixture of carbonyldihydridotris(triphenylphosphine)ruthenium (0.275 g, 0.30 mmol) and benzotriazole (0.071 g, 0.60 mmol) in benzene (30 cm^3) was heated under reflux for 1.5 h. The pale yellow-green solution which formed was concentrated to *ca.* 10 cm^{-3} under reduced pressure and then diluted with light petroleum (b.p. 60—80 °C) whereupon the required product separated as white *microcrystals* (0.26 g, 93%), m.p. 194—196 °C (Found: C, 65.55; H, 4.35; N, 9.35. $C_{49}H_{40}N_6OP_2Ru$ requires C, 66.0; H, 4.5; N, 9.4%).

[RuH(dmbta ••• H–dmbta)(CO)(PPh$_3$)$_2$]. This was similarly prepared using 5,6-dimethylbenzotriazole (Hdmbta) hydrate. The required product separated as white *microcrystals* (0.21 g, 74%), m.p. 202—204 °C (Found: C, 67.35; H, 5.0; N, 8.7. $C_{53}H_{48}N_6OP_2Ru$ requires C, 67.15; H, 5.1; N, 8.85%).

[RuH(Cl)(Hbta)(CO)(PPh$_3$)$_2$] (*two isomers*). A suspension of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.381 g, 0.40 mmol) and benzotriazole (0.143 g, 1.20 mmol) in benzene (50 cm^3) was stirred at ambient temperature for 3 h. The resulting clear yellow solution was filtered, concentrated to *ca.* 10 cm^3 under reduced pressure without the application of heat, and then diluted with light petroleum. The product separated as white *microcrystals* (0.17 g, 53%) (Found: C, 63.75; H, 4.35; N, 5.05. $C_{43}H_{36}ClN_3OP_2Ru$ requires C, 63.8; H, 4.5; N, 5.2%).

[RuH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$] (*two isomers*). This was similarly prepared using 5,6-dimethylbenzotriazole hydrate.

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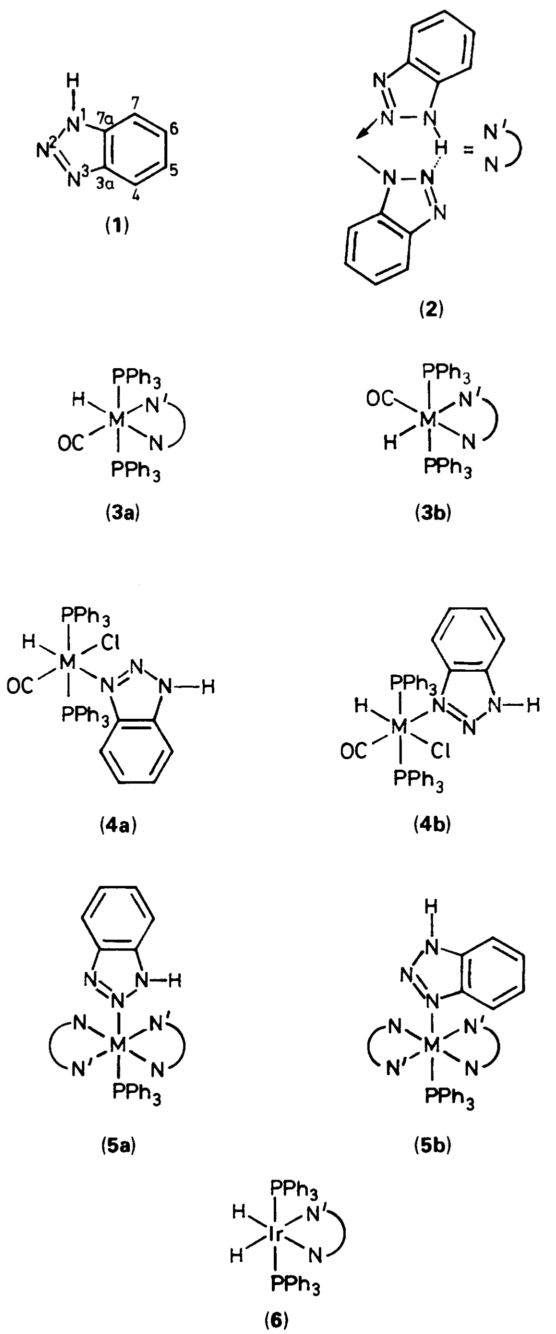
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme.

The product separated as white *microcrystals* (0.23 g, 69%) (Found: C, 64.35; H, 4.45; N, 5.0. $C_{45}H_{40}ClN_3OP_2Ru$ requires C, 64.55; H, 4.8; N, 5.0%).

[Ru(bta···H–bta)$_2$(Hbta)(PPh$_3$)]. (*a*) *From* [RuH$_2$(PPh$_3$)$_4$]. Benzotriazole (0.286 g, 2.40 mmol) and dihydridotetrakis(triphenylphosphine)ruthenium (0.346 g, 0.30 mmol) were added to degassed boiling benzene (50 cm^3). Addition of the ruthenium complex was accompanied by immediate effervescence and formation of a dark brown solution, which on heating for 2 h gradually became paler and finally turned orange. The solution was filtered and then evaporated under reduced pressure to leave an orange oil which was crystallised from dichloromethane–methanol to afford mixed isomers of the required product as pale greenish yellow *microcrystals* (0.13 g, 44%), m.p. 184—190 °C (decomp.) (Found: C, 59.65; H, 3.85; N, 21.55. $C_{48}H_{38}N_{15}PRu$ requires C, 60.25; H, 4.0; N, 21.95%).

(*b*) *From* [RuCl$_2$(PPh$_3$)$_3$]. Dichlorotris(triphenylphosphine)ruthenium (0.288 g, 0.30 mmol) was added to a solution of benzotriazole (0.286 g, 2.4 mmol) in boiling degassed toluene (50 cm^3). Triethylamine (1 cm^3) was added to the dark orange solution which immediately became paler in colour, and after heating under reflux for 3 h formed a clear orange solution. Filtration followed by evaporation under reduced pressure gave an orange residue which was identified as the required product by comparison (^{31}P-{^1H} n.m.r.) with an authentic sample prepared as described in (*a*) above.

[OsH(bta···H–bta)(CO)(PPh$_3$)$_2$]. A mixture of carbonyldihydridotris(triphenylphosphine)osmium (0.201 g, 0.20 mmol) and benzotriazole (0.071 g, 0.60 mmol) in toluene (50 cm^3) was heated under reflux for 12 h. The resulting solution was cooled, filtered, and then evaporated to dryness under reduced pressure. The residue was crystallised from benzene–light petroleum, and washed with light petroleum and ethanol to afford the product as white *microcrystals* (0.15 g, 59%), m.p. 242—243 °C (Found: C, 60.1; H, 4.1; N, 8.55. $C_{49}H_{40}N_6OOsP_2$ requires C, 60.0; H, 4.1; N, 8.55%).

[OsH(dmbta···H–dmbta)(CO)(PPh$_3$)$_2$]. This was similarly prepared using 5,6-dimethylbenzotriazole hydrate. The required product separated from benzene–hexane as very pale cream *microcrystals* (0.29 g, 72%), m.p. 243—244 °C (Found: C, 61.8; H, 4.75; N, 8.35. $C_{53}H_{48}N_6OOsP_2$ requires C, 61.4; H, 4.65; N, 8.1%).

[OsH(Cl)(Hbta)(CO)(PPh$_3$)$_2$] (*two isomers*). A suspension of carbonylchlorohydridotris(triphenylphosphine)osmium (0.312 g, 0.30 mmol) and benzotriazole (0.071 g, 0.60 mmol) in benzene (50 cm^3) was stirred at ambient temperature for 3 h. The resulting pale yellow solution was filtered, concentrated to *ca.* 10 cm^3 under reduced pressure without application of heat, and then diluted with light petroleum. The product separated as white *microcrystals* (0.18 g, 67%) (Found: C, 57.45; H, 4.0; N, 4.65. $C_{43}H_{36}ClN_3OOsP_2$ requires C, 57.5; H, 4.05; N, 4.7%).

[OsH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$] (*two isomers*). This was similarly prepared using 5,6-dimethylbenzotriazole hydrate. The product separated as white *microcrystals* (0.15 g, 54%) (Found: C, 58.4; H, 4.3; N, 4.2. $C_{45}H_{40}ClN_3OOsP_2$ requires C, 58.35; H, 4.35; N, 4.55%).

[Os(bta···H–bta)$_2$(Hbta)(PPh$_3$)] (*two isomers*). A mixture of dichlorotris(triphenylphosphine)osmium (0.314 g, 0.30 mmol), benzotriazole (0.286 g, 2.4 mmol), and triethylamine (1 cm^3) in degassed toluene (50 cm^3) was heated under reflux for 24 h to form a dark brown solution. After cooling and filtering the solution was evaporated to dryness under reduced pressure and the residue was crystallised from dichloromethane–methanol to afford the product as orange *microcrystals* (0.24 g, 67%) (Found: C, 55.1; H, 3.65; N, 20.2. $C_{48}H_{38}N_{15}OsP$ requires C, 55.1; H, 3.65; N, 20.1%).

[Os(dmbta···H–dmbta)$_2$(dmbta)(PPh$_3$)] (*two isomers*). This was similarly prepared using 5,6-dimethylbenzotriazole hydrate. The crude product separated as yellow *microcrystals* (0.20 g, 56%) (Found: C, 59.5; H, 5.0; N, 19.55. $C_{58}H_{58}N_{15}OsP$ requires C, 58.7; H, 4.95; N, 17.7%). Recrystallisation from dichloromethane–methanol afforded a dichloromethane solvate as yellow *crystals* (Found: C, 56.1; H, 4.55; N, 16.6. $C_{58}H_{58}N_{15}OsP{\cdot}CH_2Cl_2$ requires C, 55.75; H, 4.75; N, 16.55%).

[Ir(bta)(CO)(PPh$_3$)$_2$]. A mixture of *trans*-carbonylchlorobis(triphenylphosphine)iridium (0.312 g, 0.40 mmol), benzotriazole (0.48 g, 0.40 mmol), and triethylamine (1 cm^3) in benzene (50 cm^3) was heated under reflux for 30 min to form an orange suspension. The suspension was filtered and evaporated to dryness under reduced pressure and the residue crystallised from benzene–light petroleum, then washed with ethanol and light petroleum to give the product as yellow *microcrystals* (0.16 g, 46%). The product gave spectral details identical to those reported.[7]

$[IrH_2(bta\cdots H\text{–}bta)(PPh_3)_2]$. A mixture of *mer*-trihydridotris(triphenylphosphine)iridium (0.246 g, 0.25 mmol) and benzotriazole (0.089 g, 0.75 mmol) in toluene (50 cm^3) was heated under reflux for 3 h, during which time the initial pale yellow solution became colourless. The filtered solution was evaporated to dryness under reduced pressure and the residue crystallised from toluene–ethanol, then washed with ethanol and hexane to give the product as white *microcrystals* (0.12 g, 50%) m.p. 175—176 °C (Found: C, 60.2; H, 4.55; N, 8.4. $C_{48}H_{41}IrN_6P_2$ requires C, 60.3; H, 4.3; N, 8.8%).

cis-$[Pt(bta)_2(PPh_3)_2]$. A mixture of tetrakis(triphenylphosphine)platinum (0.498 g, 0.40 mmol) and benzotriazole (0.143 g, 1.20 mmol) in degassed toluene (100 cm^3) was heated under reflux for 4 h to give a pale yellow solution. After filtering, the solution was concentrated to *ca.* 10 cm^3 under reduced pressure and diluted with ethanol (10 cm^3). The resulting precipitate was filtered off and washed with ethanol and hexane to yield the desired product as white *microcrystals* (0.27 g, 71%), m.p. 215—218 °C (Found: C, 59.6; H, 3.95; N, 8.75. $C_{48}H_{38}N_6P_2Pt$ requires C, 60.3; H, 4.0; N, 8.8%).

Crystallography.—Crystals were obtained from benzene–light petroleum (b.p. 60—80 °C) solution.

Crystal data for $[OsH(bta\cdots H\text{–}bta)(CO)(PPh_3)_2]$. $C_{49}H_{40}N_6OOsP_2$, $M = 981.042$, triclinic, $a = 10.059(4)$, $b = 11.876(1)$, $c = 20.629(3)$ Å, $\alpha = 74.57(1)$, $\beta = 83.08(2)$, $\gamma = 65.96(2)°$, $U = 2\,169$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.502$ g cm^{-3}, $F(000) = 980$, $\mu(Mo\text{-}K_\alpha) = 29.1\ cm^{-1}$.

Data Collection. Intensity data were recorded on an Enraf-Nonius CAD 4 diffractometer in a standard manner, using Mo-K_α [graphite monochromatised, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å] and an ω—2θ scan mode[8] with $1.5 < \theta < 25.0$. An empirical absorption correction based on azimuthal scans was applied. A total of 8 048 reflections were recorded, of which 7 608 were unique and 6 535 satisfied the condition $I > 1.5\sigma(I)$.

Structure solution. The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares. Non-hydrogen atoms anisotropic, all hydrogens freely isotropic, the Os-H distance was fixed at 1.60 Å for stable refinement. Final $R = 0.032$, $R' = 0.034$, 692 parameters, unit weights. Atomic positional parameters are given in Table 1, selected bond distances and angles in Table 2.

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

Results and Discussion

Reactions of $[RuH_2(CO)(PPh_3)_3]$.—Treatment of $[RuH_2(CO)(PPh_3)_3]$ with benzotriazole (molar ratio 1:2) in boiling benzene for 1.5 h affords $[RuH(bta\cdots H\text{–}bta)(CO)(PPh_3)_2]$ as white microcrystals. N.m.r. data (Table 3) show a triplet hydride signal indicating a hydride *cis* to two mutually *trans* triphenylphosphines. We therefore propose the stereochemistry shown (**3a**), in which the small hydride ligand is *cis* to the most bulky side of the bta ··· H–bta ligand. This stereochemistry has been established for the analogous osmium complex by *X*-ray diffraction methods (see below). Examination of the crude reaction mixture by n.m.r. spectroscopy revealed the presence of two minor hydride species [10%, $\delta(^{31}P)$ 45.0(s) and 44.6(s) p.p.m.; hydrides, δ −10.89(t), $^2J(PH)$ 19 Hz, and −11.50(t), $^2J(PH)$ 20 Hz] which were not positively identified.

These minor components both exhibit very similar ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. signals to those of the main compoment and the hydrides and phosphorus atoms must therefore be in almost identical environments. One is likely to be an isomer (**3b**), identical with (**3a**) except that the position of the hydride and carbonyl are transposed; although the hydride is most likely to be *cis* to the most bulky side of the bta ··· H–bta, carbonyl is also a small ligand and could easily occupy this position.

The other species present could be similar to (**3a**) but with the Hbta ligand co-ordinated through N^2 rather than N^3, and with the hydrogen-bonding interaction being of an inter- rather than intra-molecular nature.

A reaction with 5,6-dimethylbenzotriazole under similar conditions but using a reflux time of 2 h affords the analogous complex $[RuH(dmbta\cdots H\text{–}dmbta)(CO)(PPh_3)_2]$ as white microcrystals. Examination of the crude reaction mixture by n.m.r. spectroscopy (Table 4) showed the presence of a similar triplet hydride signal to that seen above and again revealed the presence of two minor hydride components [$\delta(^{31}P)$ 44.60(s) and 44.2(s) p.p.m.; hydrides δ −10.86(t), $^2J(PH)$ 19, and −11.54(t), $^2J(PH)$ 19 Hz].

Reactions of $[RuH(Cl)(CO)(PPh_3)_3]$.—Treatment of $[RuH(Cl)(CO)(PPh_3)_3]$ with benzotriazole (molar ratio 1:3) in benzene at ambient temperature for 3 h affords two isomeric products $[RuH(Cl)(CO)(Hbta)(PPh_3)_2]$, in a *ca.* 85:15 ratio. N.m.r. data (Table 3) clearly indicate that both have a pair of equivalent triphenylphosphine ligands *cis* to a hydride ligand and are taken to indicate the stereochemical arrangements (**4a**) and (**4b**). The possibility that linkage isomerism is involved with benzotriazole bonding through N^2 or N^3 is improbable because the hydride chemical shifts (Table 3) are very different and seem more likely to reflect the difference between hydride *trans* to N and hydride *trans* to Cl than a difference between hydrides *trans* to very similar N-donors. Further confirmation is provided by the n.m.r. data for the analogous pairs of compounds formed under similar conditions with the monofunctional N-donor ligands pyridine and piperidine $[RuH(Cl)L(CO)(PPh_3)_2]$ [$L = C_5H_5N$, $\delta(RuH) = -13.51$(t), $^2J(PH)$ 20, $\delta(PPh_3)$ 45.8; $\delta(RuH)$ −12.41(t), $^2J(PH)$ 20 Hz, $\delta(PPh_3)$ 43.4 p.p.m.; $L = C_5H_{11}N$, $\delta(RuH)$ −13.76(t), $^2J(PH)$ 18, $\delta(PPh_3)$ 46.9; $\delta(RuH)$ −12.25(t), $^2J(PH)$ 20 Hz, $\delta(PPh_3)$ 44.6 p.p.m.].[9] Formation of these mixed isomers is thought to involve displacement of the labile triphenylphosphine ligand *trans* to hydride by the benzotriazole followed by partial isomerisation of the product, (**4a**) $\longrightarrow$ (**4b**). We have previously reported behaviour of this type involving pyridine-2-thiol and $[RuH(Cl)(CO)(PPh_3)_3]$.[5]

A reaction with 5,6-dimethylbenzotriazole under similar conditions affords the analogous isomeric products $[RuH(Cl)(CO)(Hdmbta)(PPh_3)_2]$, also in a 85:15 proportion.

Reaction of $[RuH_2(PPh_3)_4]$.—Treatment of $[RuH_2(PPh_3)_4]$ with Hbta in refluxing degassed benzene for 2 h produces two isomers of $[Ru(bta\cdots H\text{–}bta)_2(Hbta)(PPh_3)]$ in a 60:40 ratio as pale greenish yellow microcrystals. The ^{31}P n.m.r. spectrum (Table 5) exhibits two singlets which are close together indicating similar environments for the phosphorus atoms. The main item of interest in the ^1H n.m.r. spectrum is a very broad resonance at δ *ca.* 18.2 which we attribute to a hydrogen bonded proton in two bta ··· H–bta chelate ligands. The two isomers are, we believe, caused by the neutral benzotriazole ligand which can bond through either N^2 or N^3. We therefore assign structures (**5a**) and (**5b**) to this isomer pair. The NH proton of the neutral benzotriazole was not observed; it would be expected to give a broad signal and there is a possibility of exchange between bonding through N^2 and N^3. The n.m.r. data do not exclude the possibility that one of the chelate bta ··· H–bta ligands could be reversed, but this arrangement

Table 1. Fractional atomic co-ordinates (× 10^4) for [OsH(bta ··· H–bta)(CO)(PPh$_3$)$_2$]

	x	*y*	*z*		*x*	*y*	*z*
Os	−880(1)	7 753(1)	7 593(1)	C(32)	499(9)	3 111(6)	7 373(5)
C(1)	800(5)	6 644(5)	8 033(2)	C(33)	363(10)	2 785(8)	6 805(6)
O	1 891(4)	5 913(4)	8 303(2)	C(34)	94(11)	3 621(8)	6 211(5)
N(1)	−2 829(4)	9 103(4)	7 055(2)	C(35)	−35(8)	4 870(6)	6 158(4)
N(2)	−4 092(4)	8 924(4)	7 122(2)	C(40)	−891(5)	7 749(4)	5 888(2)
N(3)	−5 135(4)	9 870(4)	6 749(2)	C(41)	−2 325(6)	7 874(5)	5 846(3)
C(4)	−4 548(6)	10 717(5)	6 411(3)	C(42)	−3 115(6)	8 611(6)	5 278(3)
C(5)	−5 166(8)	11 883(5)	5 932(3)	C(43)	−2 523(7)	9 224(6)	4 741(3)
C(6)	−4 303(9)	12 511(6)	5 669(3)	C(44)	−1 097(7)	9 099(5)	4 785(3)
C(7)	−2 834(8)	12 029(6)	5 866(4)	C(45)	−287(6)	8 361(5)	5 352(3)
C(8)	−2 210(6)	10 914(5)	6 332(3)	P(2)	−1 367(1)	8 950(1)	8 401(1)
C(9)	−3 083(5)	10 232(4)	6 598(2)	C(50)	236(6)	9 194(6)	8 574(3)
N(10)	−3 433(4)	6 838(4)	8 084(2)	C(51)	1 270(6)	9 267(5)	8 096(3)
N(11)	−2 000(4)	6 553(4)	8 146(2)	C(52)	2 470(6)	9 501(6)	8 225(4)
N(12)	−1 425(5)	5 507(5)	8 601(2)	C(53)	2 613(8)	9 636(9)	8 829(5)
C(13)	−2 510(6)	5 079(6)	8 849(3)	C(54)	1 600(12)	9 587(13)	9 300(4)
C(14)	−2 486(8)	4 017(7)	9 349(4)	C(55)	429(11)	9 332(13)	9 192(5)
C(15)	−3 781(9)	3 871(8)	9 489(4)	C(60)	−2 764(6)	10 560(5)	8 196(3)
C(16)	−5 042(8)	4 715(8)	9 158(4)	C(61)	−4 179(6)	10 726(6)	8 086(3)
C(17)	−5 093(7)	5 756(7)	8 676(4)	C(62)	−5 249(8)	11 936(8)	7 908(3)
C(18)	−3 783(6)	5 929(5)	8 520(3)	C(63)	−4 930(11)	12 989(7)	8 836(4)
P(1)	45(1)	6 817(1)	6 675(1)	C(64)	−3 558(13)	12 818(9)	7 931(6)
C(20)	1 968(5)	6 578(4)	6 503(2)	C(65)	−2 453(9)	11 620(6)	8 113(4)
C(21)	2 989(6)	5 463(5)	6 374(3)	C(70)	−1 882(5)	8 263(5)	9 244(2)
C(22)	4 447(7)	5 299(6)	6 278(4)	C(71)	−970(7)	7 071(7)	9 574(3)
C(23)	4 898(6)	6 218(6)	6 323(4)	C(72)	−1 263(8)	6 487(7)	10 216(3)
C(24)	3 889(6)	7 341(6)	6 436(3)	C(73)	−2 509(8)	7 080(7)	10 538(3)
C(25)	2 436(6)	7 522(5)	6 537(3)	C(74)	−3 454(9)	8 241(7)	10 220(4)
C(30)	105(5)	5 232(5)	6 720(3)	C(75)	−3 137(8)	8 850(6)	9 577(4)
C(31)	367(7)	4 358(5)	7 330(4)				

Table 2. Selected bond distances (Å) and bond angles (°) for [Os-*H*(bta ··· *H*–bta)(CO)(PPh$_3$)$_2$]

H(1)–Os	1.592(53)	N(1)–N(2)	1.358(8)
C(1)–Os	1.825(6)	N(2)–N(3)	1.315(6)
N(1)–Os	2.160(5)	N(10)–N(11)	1.354(7)
N(11)–Os	2.176(7)	N(11)–N(12)	1.297(6)
P(1)–Os	2.354(3)	N(10) ··· H(10)	1.265(66)
P(2)–Os	2.353(4)	N(2) ··· H(10)	1.474(76)
C(1)–O	1.176(6)		
N(1)–Os–C(1)	178.1(2)	N(11)–Os–C(1)	90.0(3)
N(11)–Os–N(1)	91.8(2)	P(1)–Os–C(1)	87.8(3)
P(1)–Os–N(1)	91.8(2)	P(1)–Os–N(11)	99.9(2)
P(2)–Os–C(1)	88.7(3)	P(2)–Os–N(1)	91.2(2)
P(2)–Os–N(11)	94.9(2)	P(2)–Os–P(1)	164.8(1)
H(1)–Os–C(1)	110.1(23)	H(1)–Os–N(1)	68.0(23)
H(1)–Os–N(11)	157.9(24)	H(1)–Os–P(1)	72.9(20)
H(1)–Os–P(2)	94.4(21)	O–C(1)–Os	178.2(5)
N(2)–N(1)–Os	123.0(4)	N(3)–N(2)–N(1)	112.4(5)
H(10) ··· N(2)–N(1)	114.9(33)	H(10) ··· N(2)–N(3)	132.6(32)
N(10) ··· H(10) ··· N(2)	146.3(80)	N(10)–N(11)–Os	124.0(4)
N(12)–N(11)–Os	125.5(5)	N(12)–N(11)–N(10)	110.4(5)

would involve two of the bulky benzotriazoles being *cis* to each other, and therefore seems unlikely.

Reaction of [RuCl$_2$(PPh$_3$)$_3$].—Treatment of [RuCl$_2$(PPh$_3$)$_3$] with Hbta (1:8) and excess of triethylamine in refluxing toluene for 3 h yields a yellow powder. This was shown to be a 75:25 mixture of the two isomers of [Ru(bta ··· H–bta)$_2$(Hbta)(PPh$_3$)] as prepared from [RuH$_2$(PPh$_3$)$_4$] (see above).

Reactions of [OsH$_2$(CO)(PPh$_3$)$_3$].—Treatment of [OsH$_2$(CO)(PPh$_3$)$_3$] with benzotriazole (molar ratio 1:3) in refluxing toluene for 12 h affords [OsH(bta ··· H–bta)(CO)(PPh$_3$)$_2$] as white microcrystals. An *X*-ray diffraction study (see below) confirmed the proposed stoicheiometry and established the stereochemistry (**3a**). Two further weak hydride signals were also observed δ -12.58(t), ^2J(PH) 18, and -12.04(t), ^2J(PH) 17 Hz, with corresponding ^{31}P resonances at δ(^{31}P) 18.6(s) and 18.9(s) p.p.m. We attribute these signals to products analogous to those discussed for the corresponding ruthenium reaction (see above).

A reaction with 5,6-dimethylbenzotriazole under similar conditions affords the analogous [OsH(dmbta ··· H–dmbta)(CO)(PPh$_3$)$_2$] as very pale cream microcrystals. There is also a trace of a further hydride species at δ(P) 18.2(s) p.p.m. with the hydride at δ -12.67(t), ^2J(PH) 16 Hz. We attribute this to an isomer (**3b**) of the major product with the carbonyl and hydride transposed.

Reactions of [OsH(Cl)(CO)(PPh$_3$)$_3$].—Treatment of [OsH(Cl)(CO)(PPh$_3$)$_3$] with benzotriazole (1:2) in cold benzene for 3 h yields two isomers of [OsH(Cl)(Hbta)(CO)(PPh$_3$)$_2$] in a *ca.* 60:40 ratio to which we attribute the same arrangements (**4a**) and (**4b**) as discussed for the analogous ruthenium compounds (see above).

A similar reaction with 5,6-dimethylbenzotriazole yields the analogous mixed isomers of [OsH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$] in a *ca.* 65:35 ratio. A ^{13}C n.m.r. spectrum (Table 6) of the mixed isomers clearly exhibits six aromatic and two methyl resonances for each isomer, thus showing the benzotriazole to be bonded in an unsymmetrical fashion in each isomer, presumably through N^3.

Reactions of [OsCl$_2$(PPh$_3$)$_3$].—Treatment of [OsCl$_2$(PPh$_3$)$_3$] with benzotriazole (molar ratio 1:8) and excess of triethylamine in boiling degassed toluene for 24 h affords a 60:40 ratio of two isomers of [Os(bta ··· H–bta)$_2$(Hbta)(PPh$_3$)] as yellow microcrystals. A ^{31}P n.m.r. spectrum of this

Table 3. ^{1}H n.m.r. data for compounds with benzotriazole[a]

Complex	δ(MH)	^2J(PH)	δ(NH)
benzotriazole(Hbta)[b]			*ca.* 15.2(vb)
[RuH(bta···H–bta)(CO)(PPh$_3$)$_2$]	−11.90(t)	20	19.18(s)
[RuH(Cl)(Hbta)(CO)(PPh$_3$)$_2$][c]	−13.46(t)	19	14.14(s)
[RuH(Cl)(Hbta)(CO)(PPh$_3$)$_2$][c]	−11.86(t)	21	13.01(s)
[Ru(bta···H–bta)$_2$(Hbta)(PPh$_3$)][c]			*ca.* 18.2(*b*)[d]
[Ru(bta···H–bta)$_2$(Hbta)(PPh$_3$)][c]			
[OsH(bta···H–bta)(CO)(PPh$_3$)$_2$]	−13.04(t)	17	19.29(s)
[OsH(Cl)(Hbta)(CO)(PPh$_3$)$_2$][c]	−15.57(t)	16	14.06(s)
[OsH(Cl)(Hbta)(CO)(PPh$_3$)$_2$][c]	−12.71(t)	18	12.96(s)
[Os(bta···H–bta)$_2$(Hbta)(PPh$_3$)][c]			*ca.* 18(vbr)[d]
[Os(bta···H–bta)$_2$(Hbta)(PPh$_3$)][c]			
[IrH$_2$(bta···H–bta)(PPh$_3$)$_2$][e]	−18.84(dt)	16	19.3(b)
	−20.13(dt)	16	

[a] In CDCl$_3$, coupling constants in Hz, s = singlet, t = triplet, dt = doublet of triplets, br = broad, and v = very. [b] Aromatic protons (A$_2$B$_2$) δ 7.95 and 7.40. [c] Isomer pairs, see text. [d] Hydrogen bonded protons, see text. [e] ^2J(HH) 6 Hz.

Table 4. ^{1}H N.m.r data for compounds with 5,6-dimethylbenzotriazole[a]

Complex	δ(MH)	^2J(PH)	δ(Me)[b]	δ(NH)
Hdmbta[c]			2.42	n.o.
[RuH(dmbta···H–dmbta)(CO)(PPh$_3$)$_2$]	−11.98(t)	20	2.38, 2.20, 1.98 (6) (3) (3)	18.83(s)
[RuH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$][d]	−13.43(t)	19	2.29, 2.27	13.81(s)
[RuH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$][d]	−11.96(t)	20	2.22, 2.12	12.74(s)
[OsH(dmbta···H–dmbta)(CO)(PPh$_3$)$_2$]	−13.14(t)	17	2.36, 2.20, 2.01 (6) (3) (3)	18.76(s)
[OsH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$][d]	−15.55(t)	16	2.30, 2.27	13.74(s)
[OsH(Cl)(Hdmbta)(CO)(PPh$_3$)$_2$][d]	−12.87(t)	18	2.35, 2.32	12.69(s)
[Os(dmbta···H–dmbta)$_2$(Hdmbta)(PPh$_3$)][d]			2.33, 2.20, 2.09 (15) (12) (3)	*ca.* 14(vbr)[e]
[Os(dmbta···H–dmbta)$_2$(Hdmbta)(PPh$_3$)][d]			2.33, 2.27, 2.20, 1.94 (12) (12) (3) (3)	

[a] In CDCl$_3$, coupling constants in Hz, n.o. = not observed. [b] Numbers in parentheses are integrals. [c] C^4 and C^7, δ 7.64(s). [d] Isomer pair, see text. [e] Hydrogen bonded.

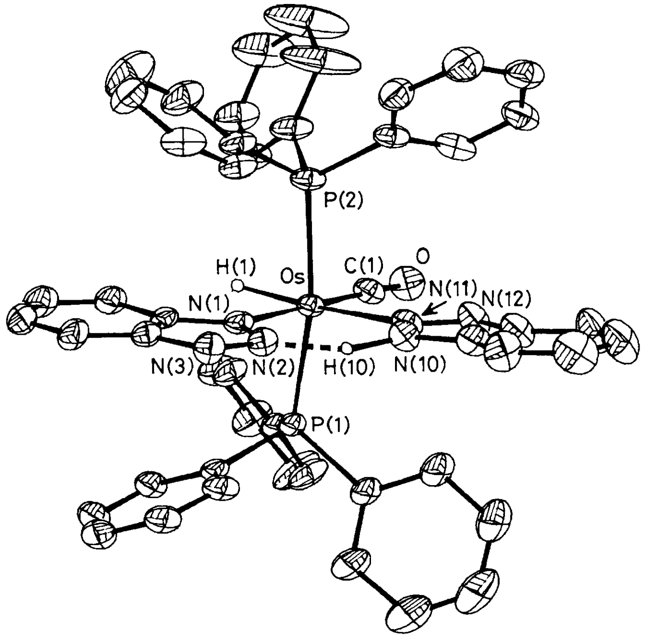


Figure. View of the molecular structure of [OsH(bta···H–bta)(CO)(PPh$_3$)$_2$] showing the atomic numbering scheme

mixture recorded at 62 °C in CDCl$_3$ shows no evidence of interchange between N^2 and N^3 bonded Hbta isomers.

Treatment of [OsCl$_2$(PPh$_3$)$_3$] with 5,6-dimethylbenzotriazole (molar ratio 1:8) and excess of triethylamine in boiling degassed toluene for 24 h affords two isomers of [Os(dmbta···H–dmbta)$_2$(Hdmbta)(PPh$_3$)] as yellow microcrystals in a 70:30 ratio. The ^{1}H n.m.r. spectrum shows a methyl region consisting of five peaks which integrate correctly for the products in the ratio given assuming that some peaks are coincident. There is also a very broad hump at δ *ca.* 14 which is attributed to the hydrogen-bonded proton and which integrates for approximately two protons.

Reactions of [IrCl(CO)(PPh$_3$)$_2$].—Treatment of [IrCl(CO)(PPh$_3$)$_2$] with Hbta (1:1) in benzene at ambient temperature for 2 h affords [IrH(Cl)(bta)(CO)(PPh$_3$)$_2$] by oxidative addition, but the product reverts to starting material on recrystallisation.

Treatment of [IrCl(CO)(PPh$_3$)$_2$] with Hbta (1:1) in the presence of excess of NEt$_3$ in refluxing benzene for 30 min affords an (85:15) mixture of *trans*-[Ir(bta)(CO)(PPh$_3$)$_2$], identical with the product obtained by Ibers and co-workers[7] and the oxidative addition product [IrH(Cl)(bta)(CO)(PPh$_3$)$_2$]. Recrystallisation gave pure [Ir(bta)(CO)(PPh$_3$)$_2$].

Reaction of mer-[IrH$_3$(PPh$_3$)$_3$].—Treatment of *mer*-[IrH$_3$(PPh$_3$)$_3$] with benzotriazole (1:3) in refluxing toluene for 3 h affords [IrH$_2$(bta···H–bta)(PPh$_3$)$_2$] as a white microcrystalline solid. The ^{1}H n.m.r. spectrum consists of two hydride signals, each of which is a triplet of doublets; this is indicative of a pair of hydrides which are mutually *cis* and which are both *cis*

Table 5. ^{31}P N.m.r.[a] and i.r.[b] data

Complex	δ(PPh_3)	ν(MH)	ν(CO)	ν(NH)
$[RuH(bta\cdots H{-}bta)(CO)(PPh_3)_2]$	43.9(s)	2 054	1 944	3 289
$[RuH(Cl)(Hbta)(CO)(PPh_3)_2]$[c]	44.4(s)	2 041	1 915	3 167
$[RuH(Cl)(Hbta)(CO)(PPh_3)_2]$[c]	45.2(s)	2 008	1 929	n.o.
$[Ru(bta\cdots H{-}bta)_2(Hbta)(PPh_3)]$[c]	44.0(s)			
$[Ru(bta\cdots H{-}bta)_2(Hbta)(PPh_3)]$[c]	42.7(s)			
$[OsH(bta\cdots H{-}bta)(CO)(PPh_3)_2]$	17.3(s)	2 140	1 934	n.o.
$[OsH(Cl)(Hbta)(CO)(PPh_3)_2]$[c]	20.0(s)	2 017	1 898	3 155
$[OsH(Cl)(Hbta)(CO)(PPh_3)_2]$[c]	18.6(s)	*ca.* 2 180	1 924	3 218
$[Os(bta\cdots H{-}bta)_2(Hbta)(PPh_3)]$[c]	2.8(s)			*ca.* 3 050
$[Os(bta\cdots H{-}bta)_2(Hbta)(PPh_3)]$[c]	1.5(s)			
$[RuH(dmbta\cdots H{-}dmbta)(CO)(PPh_3)_2]$	43.0(s)	2 034	1 948	n.o.
$[RuH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[c]	44.1(s)	2 046	1 918	3 164
$[RuH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[c]	43.9(s)	2 071	1 922	3 195
$[OsH(dmbta\cdots H{-}dmbta)(CO)(PPh_3)_2]$	16.5(s)	2 120	1 933	n.o.
$[OsH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[c]	19.5(s)	2 032	1 906	3 177
$[OsH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[c]	18.2(s)	2 149	1 927	*ca.* 3 220
$[Os(dmbta\cdots H{-}dmbta)_2(Hdmbta)(PPh_3)]$[c]	2.9(s)			*ca.* 3 150
$[Os(dmbta\cdots H{-}dmbta)_2(Hdmbta)(PPh_3)]$[c]	1.6(s)			
$[IrH(Cl)(bta)(CO)(PPh_3)_2]$	4.9(s)	n.o.	2 002	
$[Ir(bta)(CO)(PPh_3)_2]$	25.1(s)		1 954	
$[IrH(Cl)(dmbta)(CO)(PPh_3)_2]$	5.0(s)	n.o.	2 001	
$[IrH_2(bta\cdots H{-}bta)(PPh_3)_2]$	17.7(s)	2 202 2 153		
$[Pt(bta)_2(PPh_3)_2]$	5.9(s)[d]			

[a] In $CDCl_3$, shifts in p.p.m. [b] In cm^{-1}, n.o. = not observed. [c] Isomer pairs, see text. [d] $^1J(PtP)$ = 3 212 Hz.

Table 6. ^{13}C N.m.r. data for benzotriazole complexes

	Benzotriazole[a]				Phosphine				
Complex	C^{3a}, C^{7a}	C^4, C^7	C^5, C^6	Me	C^1	C^2, C^6	C^3, C^5	C^4	Carbonyl
Hbta	138.9(s)	115.0(s)	126.1(s)						
Hdmbta[b]	139.1(2)	114.6(s)	1.37.3(s)	20.6(s)					
PPh_3[c]					137.2(d) (11)	133.6(d) (20)	128.4(d) (7)	128.5(s)	
$[OsH(dmbta\cdots H{-}dmbta)(CO)(PPh_3)_2]$	142.7(s) 145.6(s)	117.0(s) 116.5(s)	131.5(s) 132.1(s)	20.7(s) 20.4(s) 20.3(s) [d]	132.9(t) (49)	133.6(t) (12)	127.4(t) (9)	129.2(s)	185.4(t) (10)
$[OsH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[e]	145.54(s) 138.1(s)	117.4(s) 108.7(s)	128.4(s) 132.2(s)	20.8(s) 20.3(s)	*ca.* 133	134.2(t) (11)	127.6(t) (9)	129.3(s)	n.o.
$[OsH(Cl)(Hdmbta)(CO)(PPh_3)_2]$[e]	145.48(s) 137.7(s)	117.1(s) 108.6(s)	128.6(s) 132.0(s)	20.7(s) 20.4(s)	*ca.* 133	134.0(t) (11)	127.5(t) (9)	129.2(s)	n.o.
$[Pt(bta)_2(PPh_3)_2]$	145.4[f] 140.5[f]	117.8(s) 113.9(s)	123.5(s) 121.3(s)		127.6(m) (39)	134.4(t) (11)	128.1(t) (11)	130.8(s)	

[a] In $CDCl_3$ except where stated. Numbers underneath resonances are coupling constants in Hz. [b] In CD_3OD. [c] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley, New York, 1972. [d] Intensity ratios 6:3:3. [e] Isomer pair, see text. [f] $^nJ(PC)$ = 2 Hz.

to a pair of mutually *trans* triphenylphosphine ligands. We therefore assign stereochemistry (**6**) to this complex. A further broad signal at δ 19.3 is attributed to the NH proton. Examination of the crude reaction mixture by n.m.r. spectroscopy revealed the presence of two further hydride species; δ(P) 18.8(s) and 18.4(s) p.p.m., δ(H) −19.31(t), $^2J(PH)$ 16 and −19.74(t), $^2J(PH)$ 16 Hz. The n.m.r. signals for these complexes are very similar to those for the major compound thus indicating a similar environment for the hydride and the phosphines; it is likely that these two species are formed from the major component by the replacement of one of the hydrides by a bta anion, thus giving rise to two possible isomers.

Reaction of $[Pt(PPh_3)_4]$.—Treatment of $[Pt(PPh_3)_4]$ with Hbta in molar ratio (1:3) in refluxing toluene for 4 h yields a white product which we formulate as $[Pt(bta)_2(PPh_3)_2]$ with a square-planar arrangement. The ^{31}P n.m.r. spectrum exhibits ^{195}Pt satellites [$^1J(PtP)$ = 3 212 Hz] which are indicative of *cis* symmetry. The ^{13}C n.m.r. spectrum exhibits six resonances for the benzotriazole ligands, which in a square-planar complex must be equivalent, and therefore this establishes that they are bound to the metal in unsymmetric fashion through N^1. The alternative N^2 symmetric co-ordination would lead to only three resonances for the benzotriazole. The ^{13}C n.m.r. resonances for the triphenylphosphine ligands show triplets for C^2 and C^3 with a coupling of 11 Hz, the resonance for C^1 consists of four lines with the inner pair more intense than the outer pair and a separation between the inner lines of 39 Hz; this is consistent with a *cis* arrangement of the phosphines.

X-*Ray Crystal Structure of* $[OsH(bta\cdots H{-}bta)(CO)(PPh_3)_2]$.—The molecular structure is shown in the Figure, molecular dimensions are given in Table 2. The monomeric complex has distorted octahedral co-ordination about the osmium atom with a chelating (N,N-donor) composite ligand *trans* to a hydride and a carbonyl with the two remaining co-ordination sites occupied by a *trans* pair of triphenylphosphine ligands. The composite ligand is formed from a neutral Hbta ligand and a bta$^-$ anion held together by a strong hydrogen bond [N(2) • • • H(10) • • • N(10)].

The most interesting feature of the structure is the short hydrogen bond between the benzotriazole nitrogen atoms N(2) and N(10) and the hydrogen atom H(10). Both of these bonds [N(2) • • • H(10) 1.474(76), N(10) • • • H(10) 1.265(66) Å] are short compared with the sum of the van der Waals radii for nitrogen and hydrogen (*ca.* 2.7 Å). The overall distance between the two nitrogen atoms N(2) • • • N(10) is *ca.* 2.62 Å which is less than the sum of the van der Waals radii for two nitrogen atoms (3.0 Å), this indicates that the hydrogen bond although bent [N(2) • • • H(10) • • • N(10) 146.3(80)°] is very strong.

These N • • • H • • • N bonds are relatively short and angular as is demonstrated by comparison with some related examples including free benzotriazole (2.81 and 2.83 Å, 167.2 and 164.8°),[9] [Cu(SO$_4$)(Hbta)$_4$·2H$_2$O] (2.73 Å),[10] imidazole–imidazolium perchlorate (2.73 Å),[11] and benzimidazole–benzimidazolium fluoroborate (2.787 Å).[12] However the bond length and in particular the bond angle will be largely governed by the chelate nature of the benzotriazole–benzotriazolate moiety and therefore cannot meaningfully be compared with data from non-cyclic systems.

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