Rhodium Complexes with 1,8-Diazabicyclo[5.4.0]undec-7-ene (dbu): Crystal Structure of *trans*-[Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$†

James V. Barkley, Craig J. Davies, Brian T. Heaton* and Chacko Jacob
Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

Attempts to deprotonate co-ordinated phenylhydrazine in *trans*-[Rh(CO)(NH$_2$NHPh)(PPh$_3$)$_2$]ClO$_4$, using 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu), resulted in the displacement of the co-ordinated hydrazine to give *trans*-[Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$ which has been fully characterised by multinuclear NMR spectroscopy and X-ray crystallography. Other rhodium(I) complexes containing dbu have also been prepared and characterised spectroscopically.

1,8-Diazabicyclo[5.4.0]undec-7-ene (dbu) has come to be commonly used in organic chemistry as the reagent of choice in many dehydrohalogenation and base-catalysed reactions, as it has been suggested to be strongly basic yet non-nucleophilic.[1] However, co-ordination of dbu to germanium and silicon has been postulated in the course of some reactions[2] and recently it has been shown to be nucleophilic towards main-group elements.[3]

In reactions with transition-metal complexes, dbu has been mainly used as a deprotonating reagent. Thus, deprotonation at the metal occurs in the reaction of [MoH(CO)$_2$(dppe)$_2$]$^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] with dbu to give [Mo(CO)$_2$(dppe)$_2$],[4] whereas ligand deprotonation occurs on reaction of dbu with hydrazine or substituted hydrazine complexes of tungsten and rhenium to give hydrazido complexes.[5] In none of these cases has dbu been found to co-ordinate to the metal. However, a rhodium complex of dbu has been reported recently[6] and we now report several complexes of rhodium containing dbu as a ligand.

Addition of dbu to *trans*-[Rh(CO)(NH$_2$NHPh)(PPh$_3$)$_2$]ClO$_4$[7] **1** in an attempt to deprotonate the co-ordinated phenylhydrazine results in displacement of NH$_2$NHPh and co-ordination of dbu to give *trans*-[Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$ **2** which can be more conveniently prepared by displacement of the perchlorato group from *trans*-[Rh(CO)(OClO$_3$)(PPh$_3$)$_2$].

Analogous rhodium(I) complexes containing dbu are reported together with their characterisation by NMR spectroscopy. In the case of *trans*-[Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$, the crystal structure has been determined and the data show that rhodium(I) behaves in a similar manner to H$^+$.

Experimental

The NMR measurements were performed on Bruker WM 200 and AMX 400 spectrometers. The ^{15}N-{^{1}H} NMR data were obtained on the AMX 400 instrument using the INEPTRD (insensitive nuclei enhanced by polarisation transfer refocussed and decoupled) pulse sequence.[8] All solutions were prepared under a nitrogen atmosphere using standard Schlenk-line techniques and all solvents were distilled from standard drying agents before use. Chemical shifts are quoted relative to MeNO$_2$ (^{15}N) and 85% H$_3$PO$_4$ in D$_2$O (^{31}P).

The complexes *trans*-[Rh(CO)(OClO$_3$)(PPh$_3$)$_2$],[9] [Rh$_2$Cl$_2$(PPh$_3$)$_4$][10] and [Rh(PPh$_3$)$_2$(nbd)]ClO$_4$ (nbd = norbornadiene, bicyclo[2.2.1]hepta-2,5-diene)[11] were all prepared by literature methods.

Preparation of the Complexes.—*trans*-[Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$ **2**. 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.040 cm^3, 0.26 mmol) was added to a solution of *trans*-[Rh(CO)(OClO$_3$)(PPh$_3$)$_2$] (0.2 g, 0.26 mmol) in CH$_2$Cl$_2$ (5 cm^3) and stirred. Addition of light petroleum (b.p. 40–60 °C) (20 cm^3) gave complex **2** as a yellow precipitate (Found: C, 60.65; H, 5.20; N, 3.05. C$_{46}$H$_{46}$ClN$_2$O$_5$P$_2$Rh requires C, 60.90; H, 5.10; N, 3.10%).

cis-[RhCl(dbu)(PPh$_3$)$_2$] **3**. 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.045 cm^3, 0.30 mmol) was added to a suspension of [Rh$_2$Cl$_2$(PPh$_3$)$_4$] (0.4 g, 0.30 mmol) in CH$_2$Cl$_2$ (5 cm^3). Addition of light petroleum (b.p. 40–60 °C) (20 cm^3) gave complex **3** as a yellow precipitate (Found: C, 64.90; H, 6.00; N, 3.60. C$_{45}$H$_{46}$ClN$_2$P$_2$Rh requires C, 66.30; H, 5.70; N, 3.45%).

cis-[Rh(dbu)$_2$(PPh$_3$)$_2$]ClO$_4$ **4**. Hydrogen was bubbled through a solution of [Rh(PPh$_3$)$_2$(nbd)]ClO$_4$ (0.4 g, 0.49 mmol) in acetone (5 cm^3) for 5 min, then dbu (0.15 cm^3, 0.98 mmol) was added. Addition of light petroleum (b.p. 40–60 °C) (20 cm^3) gave complex **4** as an orange precipitate (Found: C, 62.70; H, 6.30; N, 5.10. C$_{54}$H$_{62}$ClN$_4$O$_4$P$_2$Rh requires C, 62.90; H, 6.05; N, 5.45%).

[Rh(PPh$_3$)(dbu)(nbd)]ClO$_4$ **5**. 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.07 cm^3, 0.49 mmol) was added to a solution of [Rh(PPh$_3$)$_2$(nbd)]ClO$_4$ (0.4 g, 0.49 mmol) in acetone (5 cm^3). Addition of light petroleum (b.p. 40–60 °C) (20 cm^3) gave complex **5** as an orange precipitate (Found: C, 57.25; H, 5.50; N, 3.80. C$_{34}$H$_{39}$ClN$_2$O$_4$PRh requires C, 57.60; H, 5.55; N, 3.95%).

X-Ray Crystallography.—X-Ray diffraction data were recorded on a Rigaku AFC-6S diffractometer operating in the ω-scan mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), following standard procedures.

Crystal data. [Rh(CO)(dbu)(PPh$_3$)$_2$]ClO$_4$ **2**, C$_{46}$H$_{46}$ClN$_2$O$_5$P$_2$Rh, M = 907.2, yellow prism (0.25 × 0.15 × 0.3 mm), monoclinic, space group $P2_1/n$ (no. 14), a = 12.26(1), b = 19.503(8), c = 18.207(8) Å, β = 96.31(5)°, U = 4327 Å^3, Z = 4, D_c = 1.392 g cm^{-3}, F(000) = 1872, μ(Mo-Kα) = 5.68 cm^{-1}.

8255 Reflections were recorded ($2\theta_{max}$ = 50°) of which 4250 with $I > 3.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods (SHELX 86).[12] Full-matrix least-squares refinement converged to R and R' factors of 0.058 and 0.057 respectively and the weighting scheme was based on $(|F_o| - |F_c|)^2/|F_o|$; all non-hydrogen atoms were refined

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† *Supplementary Data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Atomic coordinates for $[\mathrm{Rh(CO)(dbu)(PPh_3)_2}]\mathrm{ClO_4}$

Atom	*x*	*y*	*z*
Rh	0.271 97(5)	0.255 44(3)	0.215 70(3)
Cl	0.618 9(4)	0.015 8(2)	0.226 7(2)
P(1)	0.336 3(2)	0.277 1(1)	0.101 8(1)
P(2)	0.195 2(2)	0.224 5(1)	0.322 7(1)
O(1)	0.099 2(5)	0.171 8(3)	0.132 5(3)
O(2)	0.572 1(9)	0.075 8(5)	0.242 2(5)
O(3)	0.539(1)	−0.032 9(5)	0.201 7(6)
O(4)	0.683(2)	−0.003 9(6)	0.281 9(7)
O(5)	0.678(1)	0.023 2(9)	0.165(1)
N(1)	0.409 8(5)	0.302 5(4)	0.274 3(4)
N(2)	0.513 1(6)	0.400 4(4)	0.312 1(4)
C(1)	0.164 5(8)	0.204 3(4)	0.164 8(4)
C(2)	0.359 2(6)	0.196 3(4)	0.053 6(4)
C(3)	0.351 9(6)	0.191 1(4)	−0.022 2(4)
C(4)	0.368 4(7)	0.128 4(5)	−0.054 9(5)
C(5)	0.394 5(8)	0.072 1(5)	−0.011 8(6)
C(6)	0.406 7(8)	0.078 0(5)	0.064 2(6)
C(7)	0.389 1(7)	0.139 7(4)	0.096 4(5)
C(8)	0.465 8(7)	0.323 3(4)	0.103 6(4)
C(9)	0.467 7(8)	0.394 0(5)	0.117 8(5)
C(10)	0.566(1)	0.428 4(5)	0.124 2(6)
C(11)	0.663(1)	0.392 2(7)	0.116 1(6)
C(12)	0.659 2(8)	0.324 7(6)	0.102 1(5)
C(13)	0.562 2(7)	0.288 9(5)	0.095 5(4)
C(14)	0.242 3(7)	0.325 9(4)	0.037 0(4)
C(15)	0.280 8(7)	0.357 7(5)	−0.024 3(5)
C(16)	0.207(1)	0.393 0(5)	−0.073 8(5)
C(17)	0.098(1)	0.394 8(6)	−0.065 1(6)
C(18)	0.060 9(7)	0.364 5(5)	−0.005 8(6)
C(19)	0.132 5(7)	0.329 9(4)	0.045 7(5)
C(20)	0.235 9(6)	0.138 6(4)	0.354 9(4)
C(21)	0.304 7(7)	0.100 7(4)	0.313 8(5)
C(22)	0.337 7(8)	0.036 7(5)	0.337 9(6)
C(23)	0.303(1)	0.011 1(5)	0.402 0(7)
C(24)	0.237(1)	0.048 1(6)	0.442 4(6)
C(25)	0.202 5(9)	0.111 5(5)	0.418 9(5)
C(26)	0.045 9(7)	0.221 8(5)	0.303 2(4)
C(27)	−0.014 2(8)	0.161 8(6)	0.300 9(5)
C(28)	−0.123(1)	0.161 5(8)	0.274 0(7)
C(29)	−0.174(1)	0.218(1)	0.251 5(8)
C(30)	−0.118(1)	0.278 6(8)	0.252 2(6)
C(31)	−0.006 5(8)	0.281 0(6)	0.276 8(5)
C(32)	0.225 0(7)	0.274 0(4)	0.407 6(4)
C(33)	0.329 6(7)	0.270 1(4)	0.443 8(5)
C(34)	0.360 1(8)	0.306 7(5)	0.506 8(5)
C(35)	0.283(1)	0.348 1(6)	0.536 5(5)
C(36)	0.178 7(8)	0.353 0(5)	0.501 7(5)
C(37)	0.149 9(7)	0.316 1(5)	0.436 3(5)
C(38)	0.507 0(7)	0.258 3(5)	0.288 8(4)
C(39)	0.589 1(7)	0.288 0(5)	0.349 8(5)
C(40)	0.614 0(8)	0.358 3(6)	0.331 0(6)
C(41)	0.420 3(6)	0.368 6(4)	0.286 2(4)
C(42)	0.315 9(8)	0.410 6(5)	0.274 4(5)
C(43)	0.286 5(8)	0.447 4(5)	0.341 6(6)
C(44)	0.349(1)	0.509 3(6)	0.366 1(7)
C(45)	0.472(1)	0.501 1(6)	0.384 4(7)
C(46)	0.528 9(9)	0.471 4(5)	0.319 9(6)

Table 2 Selected bond lengths (Å) and angles (°) for $[\mathrm{Rh(CO)(dbu)(PPh_3)_2}]\mathrm{ClO_4}$

Rh–P(1)	2.336(2)	Rh–C(1)	1.82(1)
Rh–P(2)	2.334(2)	N(1)–C(41)	1.311(9)
Rh–N(1)	2.107(7)	N(2)–C(41)	1.34(1)
P(1)–Rh–P(2)	173.63(8)	N(1)–C(41)–N(2)	125.4(8)
P(1)–Rh–N(1)	92.3(2)	C(38)–N(1)–C(41)	118.9(8)
P(1)–Rh–C(1)	86.7(3)	N(2)–C(41)–C(42)	118.2(8)
N(1)–Rh–C(1)	172.2(3)	C(40)–N(2)–C(41)	118.6(8)
Rh–N(1)–C(38)	115.1(6)	C(40)–N(2)–C(46)	114.7(8)
Rh–N(1)–C(41)	124.8(6)	C(41)–N(2)–C(46)	126.6(9)
N(1)–C(41)–C(42)	116.2(8)		

anisotropically. Atom coordinates are given in Table 1 with selected bond lengths and angles in Table 2.

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

Results and Discussion

Despite the widespread use of dbu as a deprotonating reagent, only one metal complex containing dbu as a ligand has so far been reported.[6] We now find that dbu acts as a normal nitrogen-donor ligand to rhodium(I) and report a variety of dbu complexes prepared using standard preparative methods. Thus, perchlorato displacement from *trans*-$[\mathrm{Rh(CO)(OClO_3)(PPh_3)_2}]$ readily occurs on reaction with dbu [equation (1)]. The

$$\textit{trans}\text{-}[\mathrm{Rh(CO)(OClO_3)(PPh_3)_2}] + \mathrm{dbu} \longrightarrow \textit{trans}\text{-}[\mathrm{Rh(CO)(dbu)(PPh_3)_2}]\mathrm{ClO_4} \quad (1)$$

2

complex $[\mathrm{Rh_2Cl_2(PPh_3)_4}]$ undergoes bridge-cleavage with a variety of ligands and reaction with dbu occurs similarly [equation (2)].

$$[\mathrm{Rh_2Cl_2(PPh_3)_4}] + 2\,\mathrm{dbu} \longrightarrow [\mathrm{RhCl(dbu)(PPh_3)_2}] \quad (2)$$

3

Displacement of norbornadiene from $[\mathrm{Rh(PPh_3)_2(nbd)}]\mathrm{ClO_4}$ occurs readily on reaction with H_2[11] and we now find that, on carrying out this reaction in the presence of dbu (2 mol), $[\mathrm{Rh(PPh_3)_2(dbu)_2}]\mathrm{ClO_4}$ is formed [equation (3)]. This

$$[\mathrm{Rh(PPh_3)_2(nbd)}]\mathrm{ClO_4} + 2\,\mathrm{dbu} \xrightarrow{H_2} [\mathrm{Rh(dbu)_2(PPh_3)_2}]\mathrm{ClO_4} \quad (3)$$

4

reaction had to be carried out in acetone, as the use of CH_2Cl_2 as a solvent resulted in chloride abstraction to give complex **3**. In the absence of H_2, we find that phosphine displacement from $[\mathrm{Rh(PPh_3)_2(nbd)}]\mathrm{ClO_4}$ occurs on reaction with dbu (1 mol) [equation (4)]. Further displacement of PPh_3 from

$$[\mathrm{Rh(PPh_3)_2(nbd)}]\mathrm{ClO_4} + \mathrm{dbu} \longrightarrow [\mathrm{Rh(PPh_3)(dbu)(nbd)}]\mathrm{ClO_4} \quad (4)$$

5

complex **5** occurs on reaction with dbu but it proved impossible to isolate or spectroscopically characterise the resulting product.

In order to confirm that dbu is indeed co-ordinated to rhodium, a single-crystal X-ray diffraction study was carried out on complex **2**. The crystal structure is shown in Fig. 1. The rhodium atom is in an approximate square-planar configuration with the nitrogen atom N(1) bonded to the rhodium. Of particular interest is the fact that the bond length N(1)–C(41) [1.311(9) Å] is almost equal to that of N(2)–C(41) [1.34(1) Å]. These bond lengths are also shorter than the other N–C bond lengths. In the previously determined crystal structure of $[\mathrm{P(NR_2)_2(dbu)}]^+$,[3] the corresponding N–C bond lengths are also almost equal. However, the very long P(1)–N(1) bond reported in this complex is not mirrored for complex **2**, since the

Table 3 The ^{31}P-{^1H} NMR data for rhodium(I) complexes containing dbu

Complex	δ_P	^1J(Rh–P)/Hz	^2J(P–P)/Hz
2 *trans*-$[Rh(CO)(dbu)(PPh_3)_2]ClO_4$[a]	29.5	133.8	
3 *cis*-$[RhCl(dbu)(PPh_3)_2]$[a]	53.5	209.8	47.0
	49.5	162.2	47.0
4 *cis*-$[Rh(dbu)_2(PPh_3)_2]ClO_4$[b]	47.1	175.8	
5 $[Rh(PPh_3)(dbu)(nbd)]ClO_4$[b]	27.2	172.3	

[a] Recorded in a solution of CH_2Cl_2 at 243 K. [b] Recorded in a solution of acetone at 243 K.

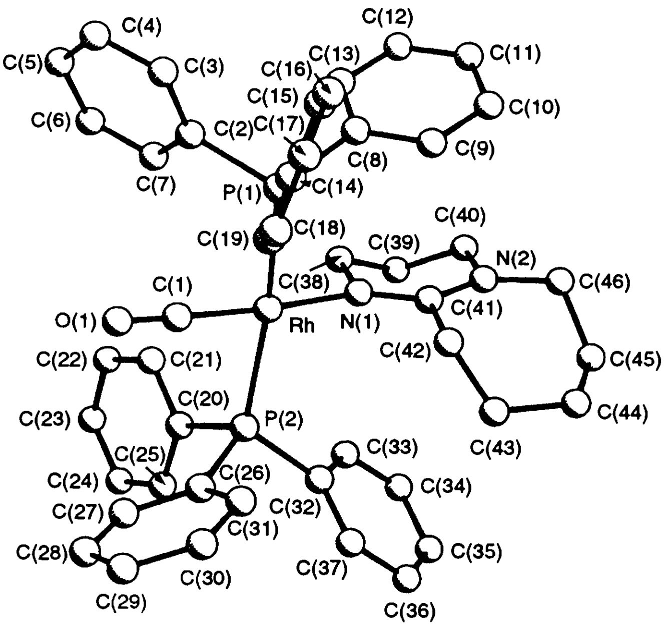
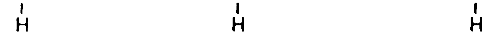


Fig. 1 Crystal structure of the cation of the square-planar complex $[Rh(CO)(dbu)(PPh_3)_2]ClO_4$

Rh–N(1) bond [2.107(7) Å] is similar to the Rh–N bond lengths found in other rhodium(I) complexes containing nitrogen-donor ligands.[6,7,13]

Nitrogen-15 NMR measurements were made on dbu and complex **2** in order to investigate the variation in δ_N on complexation. The direct ^{15}N-{^1H} NMR spectrum of neat dbu shows the presence of two resonances at δ −172 and −295 which have been assigned to N(1) and N(2) respectively since it is well established that the resonance due to sp^3 nitrogen atoms occurs at higher field than sp^2 nitrogen atoms.[14,15] The N-{^1H} NMR INEPT measurements on complex **2** show two resonances at δ −252 and −274 which have been assigned to N(1) and N(2) respectively since the former resonance appears as a doublet, *J*[RhN(1)] 17 Hz. The very large upfield shift of N(1), together with the smaller downfield shift of N(2), probably arises because of the involvement of similar canonical forms in complex **2** to those found on protonation and salt formation with organic and inorganic acids (see below).[15] This is also in agreement with the similar bond lengths found in complex **2** for N(1)–C(41) and N(2)–C(41).



Crystallographic analysis of complexes **3–5** have not been attempted since the analytical and ^{31}P-{^1H} NMR spectra are entirely consistent with the proposed formulations. The ^{31}P-{^1H} NMR data are summarised in Table 3.

In contrast to similar complexes with nitrogen-containing ligands such as pyridine,[16] rhodium(I) complexes containing dbu do not oxidatively add H_2 to give rhodium(III) hydrides. This is a surprising result which may be due to the size of the ligand, or it may be an electronic effect due to the delocalisation of the positive charge on to the ligand. In catalytic reactions where hydrogenation is an unwelcome side-reaction,[16] these complexes may prove to be useful and their catalytic potential is currently being investigated.

Acknowledgements

We thank the EPSRC for financial support (to C. J. D. and C. J.).

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Received 22nd *March* 1995; *Paper* 5/01848J