Some Metal Complexes of 2,4-Dichloro-1,3-di-t-butyldiazadiphosphetidine

By **Linda S. Jenkins** and **Gerald R. Willey,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Reactions of $(Bu^tNPCl)_2$ with $[Fe_2(CO)_9]$, $[\{RhCl(CO)_2\}_2]$, $[Mn_2(CO)_{10}]$, and $TiCl_4$ give new metal complexes incorporating the four-membered ring system as a bidentate *P*-donor. Both bridging and chelating behaviour is observed. In the case of $[Fe_2(CO)_9]$ both complexes, *i.e.* $[Fe(CO)_3\{(ClPNBu^t)_2\}]$ and $[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$, *have been isolated from tetrahydrofuran solutions depending on the presence or otherwise of a gaseous CO* atmosphere. For each complex, i.r. and ^1H and ^{31}P n.m.r. spectral information is discussed in relation to a proposed structural formulation.

CYCLOPHOSPHAZANES $(RNPX)_n$, especially the diazadiphosphetidines ($n = 2$), are now well documented.[1-13] The forerunner of these (1; X = Cl, R = Bu^t), first isolated (1969) by Scherer and Klusmann, shows a slightly puckered ring structure with chlorine atoms mutually *cis* with respect to the ring plane.[14,15] Our interest lies in its co-ordination behaviour and in a preliminary note the binuclear iron complex $[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$ (2) was described wherein (1) acts as a bidentate *P*-donor bound to separate metal atoms.[16] One other example where a diazadiphosphetidine (X = NMe_2, R = $SiMe_3$) acts as a bridging *P*-donor, in this case between two $M(CO)_5$ units (M = Cr or Mo), has been subsequently noted.[17] We now report some more metal complexes of (1).

EXPERIMENTAL

All the experiments were carried out in the absence of air. Solvents (AnalaR) were dried over molecular sieves and distilled *in vacuo* from calcium hydride and/or phosphorus pentaoxide prior to use. Enneacarbonyldi-iron (Cambrian Chemicals) and titanium tetrachloride (Fisons) were used without further purification. Decacarbonyldimanganese (Strem Chemicals) was sublimed *in vacuo* before use. Tetracarbonyldichlorodirhodium was prepared by the method of McCleverty and Wilkinson [18] and resublimed *in vacuo* before use. 2,4-Dichloro-1,3-di-t-butyldiazadiphosphetidine (1) was prepared by the method of Jefferson *et al.*[5]

Analyses were performed by Butterworths Micro Analytical Centre (B.M.A.C.), Teddington, Middlesex. Infrared spectra were recorded on Perkin-Elmer 621 and Fourier FS-720 spectrophotometers. Proton (^1H n.m.r., 90 MHz) and phosphorus (^{31}P n.m.r., 36.43 MHz) magnetic resonance spectra were recorded on a Brüker WH-90 spectrometer with $SiMe_4$ (internal) and H_3PO_4 (external) as reference standards respectively.

Preparations.—$[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$ (2). Tetrahydrofuran (thf) (*ca.* 50 cm^3) was distilled *in vacuo* on to a mixture of $[Fe_2(CO)_9]$ (1.35 g, 3.7 mmol) and (1) (1.00 g, 3.6 mmol) at 77 K in a glass ampoule (100 cm^3). After degassing, the vessel was sealed *in vacuo* and the contents allowed to warm to room temperature when a dark red solution developed. On extraction, the red solution was concentrated and transferred to a chromatography column packed with Florisil (100—200 mesh). The column was eluted with thf to give one major brown-red band which was collected and concentrated to 10 cm^3. Addition of hexane gave the pale brown semicrystalline *product* (2), yield 34%, decomposed >470 K [Found: C, 30.6; H, 2.9; Cl, 12.2; N, 5.0%; *M* (osmometric in $CHCl_3$) 576. Calc. for $C_{15}H_{18}Cl_2Fe_2N_2O_7P_2$: C, 30.9; H, 3.1; Cl, 12.2; N, 4.8%; *M* 583].

$[Fe(CO)_3\{(ClPNBu^t)_2\}]$(3). A mixture of $[Fe_2(CO)_9]$ (1.34 g, 3.68 mmol) and (1) (2.02 g, 7.36 mmol) was placed in a glass ampoule (100 cm^3) and thf (*ca.* 50 cm^3) was distilled in under vacuum at 77 K. The ampoule was filled with carbon monoxide gas (1 atm †) and sealed. A dark brown solution developed within several hours. After 3 d the solution was concentrated and transferred to a chromatography column packed with Florisil (100—200 mesh) and eluted with thf. The major brown-red band was collected and concentrated to 10 cm^3. Addition of n-hexane caused precipitation of the creamy brown solid *product* (3), yield 20% (Found: C, 31.8; H, 4.5; Cl, 16.5; N, 6.9. Calc. for $C_{11}H_{18}Cl_2FeN_2O_3P_2$: C, 31.8; H, 4.4; Cl, 17.0; N, 6.7%).

$[RhCl(CO)\{(ClPNBu^t)_2\}]$ (4). n-Hexane (*ca.* 50 cm^3) was distilled *in vacuo* on to a mixture of $[\{RhCl(CO)_2\}_2]$ (0.93 g, 2.40 mmol) and (1) (1.38 g, 5.01 mmol) at 77 K in a glass ampoule (100 cm^3). After degassing, the ampoule was sealed and allowed to warm slowly to room temperature when a slow reaction with bubbling occurred. The pale lemon solid which formed after 24 h was filtered off, washed thoroughly with n-hexane, and identified as product (4), yield 80% (Found: C, 24.2; H, 4.2; Cl, 24.1; N, 6.7. Calc. for $C_9H_{18}Cl_3N_2OP_2Rh$: C, 24.5; H, 4.1; Cl, 24.1; N, 6.3%).

$[TiCl_4\{(ClPNBu^t)_2\}]$ (5). An n-hexane solution (20 cm^3) of $TiCl_4$ (0.7 g, 3.6 mmol) was added dropwise under a nitrogen atmosphere to a similar solution of (1) (1.2 g, 4.2 mmol) contained in a glass ampoule (100 cm^3). A reaction occurred almost instantly to give an orange solution and precipitate. The orange product (5) was *immediately* filtered off, washed thoroughly with benzene and n-hexane to remove unchanged reactants, and then pumped *in vacuo* for several hours, yield 55% (Found: C, 21.1; H, 4.0; Cl, 45.3; N, 5.8. Calc. for $C_8H_{18}Cl_6N_2P_2Ti$: C, 20.7; H, 3.9; Cl, 45.8; N, 6.0%).

$[Mn(CO)\{(ClPNBu^t)_2\}_2]$ (6). A mixture of $[Mn_2(CO)_{10}]$ (3.07 g, 7.88 mmol) and (1) (2.09 g, 7.60 mmol) was placed in a round-bottomed flask (250 cm^3) fitted with a condenser and nitrogen bubbler and xylene (*ca.* 100 cm^3) was added. The initial yellow solution was heated under reflux under nitrogen for 15 min and then allowed to cool to room temperature. The solid material was filtered off and recrystallised from thf to give the product (6) as a white semicrystalline solid, yield 45% (Found: C, 34.5; H, 5.6;

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† Throughout this paper: 1 atm = 101 325 Pa.

Cl, 22.7; N, 8.9. Calc. for $C_{17}H_{36}Cl_4MnN_4OP_4$: C, 32.2; H, 5.7; Cl, 22.4; N, 8.8%).

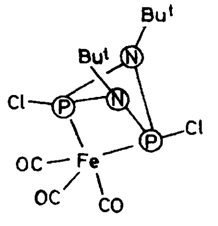
RESULTS AND DISCUSSION

Reaction with $[Fe_2(CO)_9]$ *in thf Solution.*—Extensive work, mainly by Cotton and his co-workers,[19] has demonstrated that the nature and reactivity of the $[Fe_2(CO)_9]$-thf ' solution ' is very much dependent on the presence or otherwise of gaseous CO. For example, reaction with the *S*-donor 1,3-dithiacyclohexane gives three products as a consequence of varying the gaseous atmosphere.[20] In the present instance we have observed formation of the binuclear complex (2) when the reaction was carried out in a degassed system,[16] and now formation of the new mononuclear complex $[Fe(CO)_3\{(ClPNBu^t)_2\}]$ (3) when an atmosphere of CO is maintained. The creamy brown solid (3) was isolated following separation and purification of the reaction mixture by column chromatography. A small amount of (2) and, in one case, a trace amount of a chestnut-brown solid, was also obtained; the latter has proved elusive and remains uncharacterised. Complex (3) is soluble in donor solvents but is extremely sensitive to air and moisture. The proposed structure is based on a five-co-ordinate [idealised *trans*-(C_{2v}) or *cis*-(C_s) rectangular pyramid or *cis*-(C_{2v}, C_s) trigonal bipyramid] geometry with (1) bound as a chelating *P*-donor. Spectral data (Table) support this formulation: the i.r. spectrum shows three major bands, with a weak band at 2 050 cm^{-1}, in the metal–carbonyl stretching region; the ^{1}H n.m.r. spectrum gives one methyl resonance for equivalent t-butyl groups, little altered in position to that of (1) as expected; the ^{31}P n.m.r. spectrum shows one signal shifted considerably upfield with respect to that of (1). The comparable five-co-ordinate diphosphane complex $[Fe(CO)_3(Ph_2PCH_2PPh_2)]$ [21] is a fluxional molecule whose actual structure lies between the idealised trigonal-bipyramidal and rectangular-pyramidal geometries with all three carbonyl groups non-equivalent.

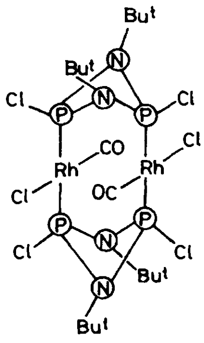
Spectral data for the metal complexes

	Compound	^{1}H N.m.r.^{a}	^{31}P N.m.r.^{b}	I.r. (cm^{-1}) ^{c}
(1)	$(Bu^tNPCl)_2$	1.40	−207.67	2 960vs, 2 930vw, 2 900w, 2 870w, 2 790m, 2 690m, 2 582m, 2 484m, 1 460s, 1 395s, 1 370s, 1 300w, 1 240s, 1 200s,br, 1 040s, 935s, 905s, 530m, 490s, 435m, 395s, 338w, 257w, 228vw, 213s
(2)	$[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$	1.48	17.08	2 960s, 2 920s, 2 880s (sh), 2 790m, 2 730m, 2 690m, 2 580m, 2 480m, 2 360vw, 2 100s, 2 070m (sh), 2 047s, 1 990s, 1 960s, 1 925s, 1 715w, 1 500m, 1 460s, 1 440s, 1 395s, 1 368s, 1 285s (sh), 1 255s (sh), 1 245vs, 1 220s, 1 180s,br, 1 060s,br, 1 015s,br, 975m,br, 930m,br, 875s,br, 795m, 715m, 680w, 675w (sh), 638m (sh), 615m, 545m,br, 440m,br 395w (sh), 340w, 280vw
(3)	$[Fe(CO)_3\{(ClPNBu^t)_2\}]$	1.33	10.46	2 960s, 2 900m, 2 860m, 2 790m, 2 700w, 2 590w, 2 400w, 2 050w, 2 000s, 1 955s, 1 925s, 1 620vw, 1 500w, 1 455w, 1 390w, 1 365m, 1 295w (sh), 1 255s, 1 220m (sh), 1 200s, 1 130w (sh), 1 100s, 1 030m (sh), 935m, 920s, 900m, 800w, 720w, 625m, 540w, 450m
(4)	$[RhCl(CO)\{(ClPNBu^t)_2\}]$	1.65	6.26, −11.51	2 970s, 2 960s, 2 950s, 2 920s, 2 860m, 2 730m, 2 020s, 2 005w, 1 960vw, 1 455s, 1 395m, 1 370s, 1 245w, 1 225w, 1 180vw, 1 160w (sh), 1 080vw, 1 045s, 1 030s, 975vw, 930w, 855s (sh), 865s, 800w, 720w, 560w (sh), 535s, 510w (sh), 455m, 425m, 392s, 348s, 272s, 255m, 188w,br
(5)	$[TiCl_4\{(ClPNBu^t)_2\}]$	1.27	20 (br)	2 960s, 2 920s, 2 880s, 2 790m,2 690m, 2 580m, 2 480m, 2 010vw, 1 625m,br, 1 590s, 1 495w, 1 470m, 1 400m, 1 370s, 1 310m, 1 290m, 1 255m, 1 175s,br, 1 040s,br, 940m, 915m, 890m, 900w, 730m, 720m, 625w, 560w, 540w, 435s, 360—345vs, 275w
(6)	$[Mn(CO)\{(ClPNBu^t)_2\}_2]$	1.0 (br)		2 995s, 2 975s, 2 950s, 2 905s, 2 890s, 2 795vw, 2 770vw, 2 310vw, 2 280vw, 1 920m, 1 870vw, 1 660m, 1 645w (sh), 1 465m, 1 455m (sh), 1 445m (sh), 1 375m, 1 350m, 1 320w, 1 300w, 1 270m, 1 255w (sh), 1 240vw (sh), 1 180m, 1 080m (sh), 1 060m (sh), 1 040vs, 960w, 925s, 895vs, 885vs (sh), 855m (sh), 805w, 730w, 680w, 465vw,br

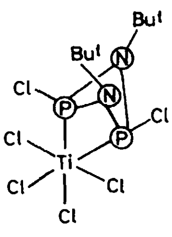
^{a} Run at room temperature in $S(CD_3)_2O$, $CDCl_3$, or CD_2Cl_2; chemical shifts (δ/p.p.m.) with respect to $SiMe_4$ (δ = 0). ^{b} Run at room temperature in $S(CD_3)_2O$ or $CDCl_3$; chemical shifts are high field (+) or low field (−) with respect to H_3PO_4 (δ = 0). ^{c} Recorded as Nujol and hexachlorobutadiene mulls between CsI plates.



(3)



(4)



(5)

With the binuclear bidentate-ligand species $[Fe_2(CO)_7(L-L)]$, bridging and chelating forms are possible. Both have been realised, *e.g.*, bridging in $[Fe_2(CO)_7(Ph_2PCH_2PPh_2)]$ [22] with one symmetrical bridging carbonyl group, and chelating in $[Fe_2(CO)_7(bipy)]$ [23] (bipy = 2,2′-bipyridyl) with one symmetrical and one unsymmetrical semi-bridging (s.b.) carbonyl group present. In the case of (2) the absence of a low-energy ν(CO) stretching mode associated with a s.b.CO group,[23,24] and the argument of less strain and implicit five- rather than four-membered ring formation, form the basis of the proposal for a bridging ligand.[16] Spectral data for (2) have been discussed previously.

Reaction with $[\{RhCl(CO)_2\}_2]$.—Prolonged treatment of the chloride-bridged dirhodium complex with (1) in n-hexane provided the pale lemon solid $[RhCl(CO)\{(ClPNBu^t)_2\}]$ (4). This decomposes to a dark orange-brown solid on the slightest exposure to air. Although solubility problems denied a molecular-weight evaluation, the proposed dimeric square-planar structure shown is supported by spectral data (Table). The room-temperature ^{31}P n.m.r. spectrum shows an upfield doublet signifying co-ordinated mutually *trans* phosphorus atoms. One single methyl resonance appears in the ^1H n.m.r. spectrum. The i.r. spectrum includes one intense metal-carbonyl stretching band (B_u mode) at 2 020 cm^{-1} with some evidence of very weak shoulders at *ca.* 2 005 and *ca.* 1 960 cm^{-1}, the last two bands probably resulting from solid-state effects. Two carbonyl bands (A_1 and B_2 modes) would be expected for the unsymmetrical *cis*-chloro-structure. In the far-i.r. region the broad intense band at 272 cm^{-1} and the associated shoulder at 255 cm^{-1} on the low-energy side are assigned as ν(RhCl) stretching modes; these fall within the 250—350 cm^{-1} range expected for square-planar neutral rhodium(I) complexes.[25] The diphosphane series, $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1, 3,$ or 4),[26,27] similarly has a *trans* configuration about the metal. In stark contrast, the iridium(I) analogue $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}][IrCl_2(CO)_2]$ is ionic.[28]

Reaction with $TiCl_4$.—Direct addition in n-hexane gives a smooth reaction with almost immediate precipitation of orange $[TiCl_4\{(ClPNBu^t)_2\}]$ formulated as the six-co-ordinate *cis* complex (5). The choice of reaction conditions, especially solvent, seems important since in several instances, *i.e.* with benzene and chloroform, we obtained an oily intractable product. Complex (5) is extremely sensitive to air and moisture and virtually insoluble in the common organic solvents. Limited solubility in dimethyl sulphoxide allowed n.m.r. measurements (Table). One sharp methyl resonance in the ^1H n.m.r. spectrum and one broadened signal to high field in the ^{31}P n.m.r. spectrum comply with the proposed bidentate phosphorus bonding. The low i.r. spectrum shows one strong, clearly multiple, band in the 345—360 cm^{-1} region consistent with six-co-ordinate Ti^{IV}. The band at 435 cm^{-1} is assigned to a ν(TiP) stretching mode *cf.* $[TiCl_4\{Ph_2P(CH_2)_2PPh_2\}]$ has[29] ν(TiP) at 453 and 414 cm^{-1}; other diphosphane complexes include $[TiCl_4\{Et_2P(CH_2)_2PEt_2\}]$ and $[TiCl_4\{Me_2P(CH_2)_2PMe_2\}]$.[30] Six-co-ordinate adducts of titanium(IV) chloride with both *N*- and *P*-donors are legion and the apparent choice between the two sites is resolved in this instance in favour of the *P*-donor. Presumably, unfavourable steric constraints and the tertiary amine character mitigate against involvement of the *N*-donor.

Reaction with $[Mn_2(CO)_{10}]$.—The reaction with $[Mn_2(CO)_{10}]$ has been attempted in several ways and, judging from the variety of products observed, is obviously complex. Based on the descriptions of phosphine and arsine derivatives of this metal carbonyl, where different products have been obtained under almost identical reaction conditions, this experience is commonplace.[24] Even the time factor can be important. Here direct reaction with a two-fold excess of (1) under reflux in xylene for 15 min gives the white complex $[Mn(CO)\{(ClPNBu^t)_2\}_2]$ (6) as the major product. This exhibits a single carbonyl-stretching frequency at 1 920 cm^{-1} in Nujol; the methyl proton resonance appears as a very broad signal poorly resolved at δ 1.0 p.p.m. We were unable to obtain a reliable ^{31}P n.m.r. spectrum. In view of the erroneous characterisation of the analogous complex $[Mn(CO)\{Ph_2P(CH_2)_2PPh_2\}_2]$[31-33] (a recent *X*-ray structure[34] confirms that the correct formulation should be $[Mn(CO)\{COC_6H_4PPh(CH_2)_2Ph_2\}\{Ph_2P(CH_2)_2PPh_2\}]$ as a diamagnetic complex containing an acyl carbonyl group linking an *ortho* carbon atom of one of the aromatic rings to the metal), the 'obvious' five-co-ordinate arrangement for (6) is couched with reservation. Although similar migration and insertion of a carbonyl group is most unlikely in this particular instance, hydride formation (ex-solvent) is a distinct possibility: $[MnH(CO)\{(ClPNBu^t)_2\}_2]$ becomes diamagnetic with the more favoured six-co-ordinate metal environment, but spectrally neither a Mn–H hydride resonance nor a stretching mode can be located. Analytically, there can be no distinction either way and further comment on (6) is reserved pending an *X*-ray structure determination.

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