

### Preliminary communication

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## (1,3-DI-*t*-BUTYL-2,4-DICHLORODIAZADIPHOSPHETIDINE)HEPTACARBONYLDIIRON: A NOVEL COMPLEX INCORPORATING A DIAZADIPHOSPHETIDINE RING SYSTEM AS A BIDENTATE P-DONOR

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### Summary

(1,3-Di-*t*-butyl-2,4-dichlorodiazadiphosphetidine)heptacarbonyldiiron has been prepared from  $\text{Fe}_2(\text{CO})_9$  and 1,3-di-*t*-butyl-2,4-dichlorodiazadiphosphetidine in THF.

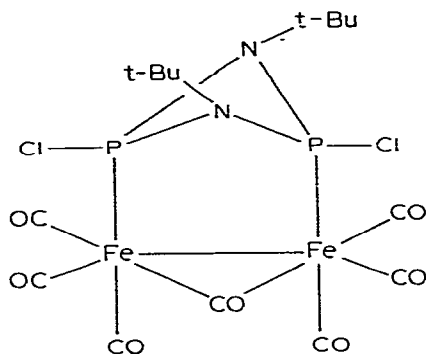
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The four-membered phosphorus(III)—nitrogen compound 1,3-di-*t*-butyl-2,4-dichlorodiazadiphosphetidine (I) [1] offers intriguing potential as a ligand. Both the phosphorus and nitrogen atoms possess formal lone pairs and, although P—N bond length comparisons imply some delocalisation around the slightly puckered ring [2], are probable  $\sigma$ -donor sites. With chlorine atoms mutually *cis* with respect to the ring plane, P-donor activity seemed to us the more likely of the two. For phosphine (and amine) ligands in general, reaction with the  $\text{Fe}_2(\text{CO})_9$ /THF system, as developed by Cotton [3–5], has proved a useful route to many new and unusual products; the same method has now been successfully used with I.

Tetrahydrofuran ( $\sim 50 \text{ cm}^3$ ) was distilled in vacuo into a mixture of  $\text{Fe}_2(\text{CO})_9$  (1.35 g; 3.7 mmol) and I (1.0 g; 3.6 mmol) maintained at 93 K in a  $100 \text{ cm}^3$  capacity glass ampoule. After de-gassing, the vessel was sealed and allowed to warm to room temperature when a dark red solution slowly developed. Extraction and concentration of the mixture after several days gave a deep red solution which provided the title compound (II) as a pale brown semi-crystalline solid (34% yield) following purification by column chromatography. Anal. found: C, 30.6; H, 2.9; Cl, 12.2; N, 5.0. mol.wt. (osmometric ( $\text{CHCl}_3$ )) 576, m.p. dec. > 470 K.  $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_7\text{P}_2\text{Fe}_2$  calcd.: C, 30.9; H, 3.1; Cl, 12.2; N, 4.8%; mol.wt. 583.

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(II)

The brown solid is soluble in chloroform, tetrahydrofuran and dichloromethane but is extremely air-moisture sensitive. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows a single broad absorption ( $\delta$  1.48 ppm; (TMS)) for the t-butyl groups with non-resolvable coupling to phosphorus. A 1/2/1 triplet ( $\delta$  1.41 ppm;  $J(^{31}\text{PNCCH})$  1.03 Hz) is observed for uncoordinated ligand. The  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) confirms coordinated phosphorus atoms in an equivalent environment; the sharp singlet of the free ligand ( $\delta$   $-207.09$  ppm;  $(\text{H}_3\text{PO}_4)$ \*) is shifted dramatically upfield and is considerably broadened ( $\delta$   $+17.08$  ppm;  $(\text{H}_3\text{PO}_4)$ ).

The structure proposed for II incorporates the diazadiphosphetidine ring system as a bridging P-donor bound to two separate metal centres and is based on that of  $[\text{Ph}_2\text{PCH}_2\text{PPh}_2]\text{Fe}_2(\text{CO})_7$  [7]. Such a structure should exhibit six infrared active  $\nu(\text{CO})$  terminal and one  $\nu(\text{CO})$  bridging modes: the infrared spectrum ( $\text{CHCl}_3$ ) of II shows strong bands at 2100, 2047, 1991, 1960, 1923 and  $1715\text{ cm}^{-1}$  respectively with a shoulder at  $\sim 2070\text{ cm}^{-1}$ .

An alternative structure based on I as a chelating P-donor bound to just one metal centre involving an unsymmetrical semi-bridging carbonyl group (SBCO), as found for  $\text{Fe}_2(\text{CO})_7$  bipyridine [8], is discounted at this stage\*\* on account of the steric strain so imposed and the absence of a  $\nu(\text{CO})$  band  $\sim 1850\text{ cm}^{-1}$  attributable to such an SBCO linkage [8,9]. Preliminary results using other "soft" acids, e.g.  $\text{Co}_2(\text{CO})_8$  and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  to promote P-donor activity are equally encouraging but attempts to involve I as an N-donor in metal coordination have been uniformly unsuccessful probably because of steric problems associated with the bulky, mutually *trans* tertiary butyl groups. Reactions using  $\text{TiCl}_4$ ,  $\text{VCl}_4$ ,  $\text{TiCl}_3 \cdot 2\text{NMe}_3$  and  $\text{CrCl}_3 \cdot 3\text{THF}$  as the appropriate "hard" acid only result in intractable oils and solids.

### Acknowledgment

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\*Jefferson et al. [6] report  $\delta$   $-210.9$  ppm ( $\text{H}_3\text{PO}_4$ ) in  $\text{CH}_2\text{Cl}_2$ .

\*\*Pending an X-ray structural analysis currently in progress.

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