Dinitrogen and Related Compounds of Molybdenum with the Tripodal Phosphines $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$ as Coligands†

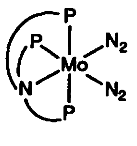
María J. Fernández-Trujillo, Manuel G. Basallote, Pedro Valerga and María C. Puerta*
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

The reduction of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ with a sodium dispersion in tetrahydrofuran (thf) under a dinitrogen atmosphere yields the unstable complex *cis*-$[Mo(N_2)_2\{N(CH_2CH_2PPh_2)_3\}]$, which decomposes in a few days even in solution under dinitrogen. Studies of the chemical reactivity of this compound towards carbon monoxide, PMe_3, MeI and CF_3CO_2H have been carried out and the complexes $[Mo(CO)_3L]$, $[Mo(PMe_3)_3L]$, $[MoI_2L]$ and $[Mo(CF_3CO_2)_2L]$ [$L = N(CH_2CH_2PPh_2)_3$] have been isolated and identified. The reduction of the analogous complex $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]$ gives unstable *trans*-$[Mo(N_2)_2\{P(CH_2CH_2PPh_2)_3\}]$. The ligand-substitution reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with $N(CH_2CH_2PPh_2)_3$ yields the complex *cis*-$[Mo(N_2)(PMe_3)\{N(CH_2CH_2PPh_2)_3\}]$.

In the last years several aspects of dinitrogen metal complexes have been studied, particularly those relevant to the biochemical action of nitrogenases. A great deal of work has been focused on complexes with transition metals in low oxidation states and mono- or bi-dentate[1] phosphine ligands. The increase in the thermodynamic stability of the complex by formation of additional chelate rings and probably also the lower ability for substitution of these phosphines have made interesting the preparation and study of dinitrogen metal complexes with polydentate ligands. The tripodal ligands $N(CH_2CH_2PPh_2)_3$ and $P(CH_2CH_2PPh_2)_3$ can potentially act in a tetradentate manner and form metal complexes with different co-ordination numbers and geometries.[2] In addition they show a relatively high chemical versatility allowing the activation of small molecules and contributing to the stabilization of chemical groups which are usually very reactive. An additional striking feature exhibited by $N(CH_2CH_2PPh_2)_3$ is its sometimes unpredictable chemical behaviour due to the several possible combinations of nitrogen and phosphorus atoms as donors.[3,4]

In a recent paper[5] we reported the synthesis and the crystal structure of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$. Since it is well known that complexes with formula $[MoCl_3L_3]$ (L = phosphine) are used as precursors in the preparation of dinitrogen complexes,[6,7] it seems interesting to explore the behaviour of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ as starting material to obtain dinitrogen and related complexes. In this paper, we report that reduction of this complex with a sodium dispersion yields *cis*-$[Mo(N_2)_2\{N(CH_2CH_2PPh_2)_3\}]$. On the other hand, the reduction reaction of the analogous complex $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]$ has also been investigated, leading to different results since it produces *trans*-$[Mo(N_2)_2\{P(CH_2CH_2PPh_2)_3\}_2]$, which is also relatively unstable, losing N_2 on standing.

A different route to the synthesis of dinitrogen complexes consists in the use of substitution reactions on well characterized dinitrogen complexes which lose one or more coligands more readily than dinitrogen[8-11] itself. In this sense we have studied the reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$[12] with $N(CH_2CH_2PPh_2)_3$, obtaining *cis*-$[Mo(N_2)(PMe_3)\{N(CH_2CH_2PPh_2)_3\}]$, in which one of the two initial dinitrogen ligands has been displaced.



A

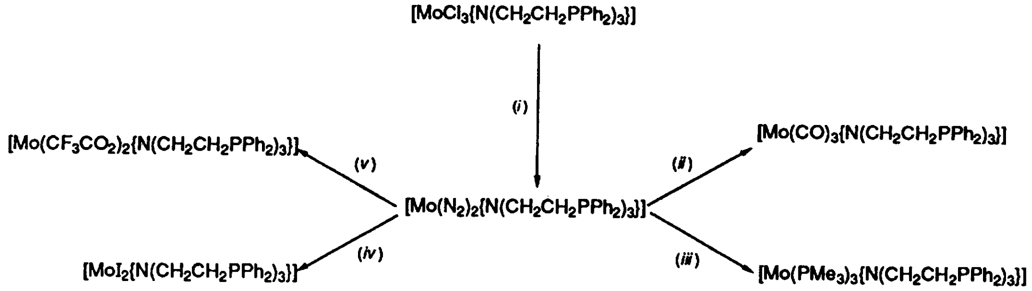
Results and Discussion

The Reduction of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ *under* N_2.—The complex $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ has been reduced with a sodium dispersion in tetrahydrofuran (thf) under a nitrogen atmosphere to give a microcrystalline bright orange compound. This material is very unstable and decomposes in hours at room temperature, even under a dinitrogen atmosphere, giving a yellow product. In solution the decomposition is slower but occurs in a few days regardless of whether a dinitrogen atmosphere is used. For this reason it is necessary to keep the product even when in its microcrystalline form in a refrigerator and under a dinitrogen atmosphere. The dinitrogen complex is soluble in benzene and thf and shows low solubility in light petroleum and diethyl ether. The IR spectrum of the orange compound in Nujol displays two intense absorption bands at 1970 and 1898 cm^{-1} [$\nu(N\equiv N)$] indicative of the formation of a *cis*-bis(dinitrogen) complex.[12] The $^{31}P-\{^1H\}$ NMR spectrum of a freshly prepared sample in thf shows a doublet at δ 55.15 (P_A) and a triplet at δ 50.28 (P_M) with $J(P_A-P_M) = 12.8$ Hz from a A_2M spin system. These data also suggest the formation of a cis-bis(dinitrogen) complex with the $N(CH_2CH_2PPh_2)_3$ ligand acting in a tetradentate manner. Thus the proposed formula for this compound is *cis*-$[Mo(N_2)_2\{N(CH_2CH_2PPh_2)_3\}]$ and a feasible structure according to spectral data is shown in **A**. The complex was further characterized by studying its chemical reactivity.

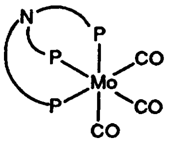
Reactivity of *cis*-$[Mo(N_2)_2\{N(CH_2CH_2PPh_2)_3\}]$ **1**.—The chemical reactivity of complex **1** is summarized in Scheme 1. The reaction of **1** with CO (p = 1 atm) in thf gave a yellow

---

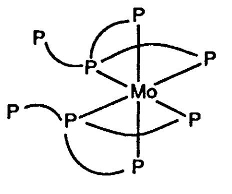
† *Non-SI unit employed:* atm = 101 325 Pa.



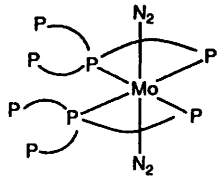
Scheme 1 (*i*) Sodium dispersion, thf, N_2; (*ii*) CO; (*iii*) excess of PMe_3; (*iv*) MeI; (*v*) CF_3CO_2H



B

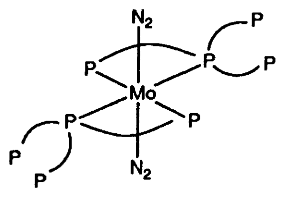


C

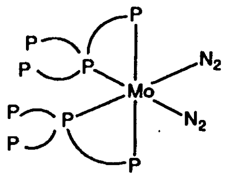


D

C **D**



E



F

crystalline product with formula $[Mo(CO)_3\{N(CH_2CH_2PPh_2)_3\}]$ **2** as inferred from analysis. It is soluble in thf and acetone, and shows low solubility in light petroleum and diethyl ether. The IR spectrum in Nujol mull shows two strong bands at 1950 and 1840 cm^{-1} which can be assigned to ν(CO) (carbonyl complex[12]). The $^{31}P-\{^1H\}$ NMR spectrum in thf shows a singlet at δ *ca.* 60. This suggests a *fac*-tricarbonyl arrangement as in the case of related tricarbonyl compounds.[13,14] The $N(CH_2CH_2PPh_2)_3$ ligand acts in a tridentate manner through the three P atoms, **B**. The described behaviour shows that this ligand acts with unusual versatility owing to the easy dissociation of the central nitrogen donor atom.[15,16] The presence of two bands in the IR spectrum in the carbonyl region is also consistent with the formulation as a *fac*-tricarbonyl complex.

The reaction of complex **1** with an excess of trimethylphosphine gave a polycrystalline orange solid. Its elemental microanalysis corresponds to the formula $[Mo(PMe_3)_3\{N(CH_2CH_2PPh_2)_3\}]$ **3**. The IR spectrum shows a strong band at 950 cm^{-1} ascribed to a PMe_3 ligand, and other bands corresponding to the co-ordinated $N(CH_2CH_2PPh_2)_3$ ligand at 1180m, 1110m and 750s cm^{-1}. No bands which can be assigned to ν(N≡N) are observed.

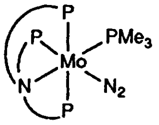
An attempt was made to alkylate the dinitrogen ligand in complex **1**. Reaction with MeI in benzene gave an orange solid, insoluble in most of the usual organic solvents, analysing for $[MoI_2\{N(CH_2CH_2PPh_2)_3\}]$ **4**. Thus, alkylation at the dinitrogen to produce an alkyldiazenide complex[17] has been avoided, and the reaction actually leads to oxidation of the metal.[14]

The reaction of complex **1** with an excess of CF_3CO_2H, in an attempt to protonate the co-ordinated dinitrogen,[18] resulted in gas evolution (probably dinitrogen). No ammonia or hydrazine was detected upon base distillation of the reaction mixture. A dark orange solid was also isolated of formula $[Mo(CF_3CO_2)_2\{N(CH_2CH_2PPh_2)_3\}]$ **5**. The IR spectrum shows bands that can be ascribed to the $N(CH_2CH_2PPh_2)_3$ ligand, a very strong band at 1680–1650 cm^{-1} corresponding to ν(C=O) and another band at 1110–1200 cm^{-1} assignable to ν(CF).

It has not been possible to obtain the NMR spectra of the products obtained by reaction of the *cis*-bis(dinitrogen) complex with PMe_3, MeI and CF_3CO_2H either because of low solubility or decomposition in the usual organic solvents.

The Reduction of $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]$ *under* N_2.—The analogous reduction of $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]$[5] with a sodium dispersion in thf under a dinitrogen atmosphere gives an orange solid similar to that of the complex with $N(CH_2CH_2PPh_2)_3$. This compound shows an intense band in the IR spectrum at 1950 cm^{-1} suggesting it is a mono(dinitrogen) or a *trans*-bis(dinitrogen) complex.[7] It is unstable and after a few days even under a nitrogen atmosphere the characteristic dinitrogen band disappears both in the solid state (Nujol) and in thf solution. It is soluble in thf and benzene and shows low solubility in light petroleum and diethyl ether.

Microanalytical data are in reasonable agreement with the composition $[Mo(N_2)_2\{P(CH_2CH_2PPh_2)_3\}]$ **6**, except for the low amount of nitrogen found. However, owing to the unstable character of this complex, this result is not unexpected. The $^{31}P-\{^1H\}$ NMR spectrum in thf shows a broad multiplet centred at δ −11.5, and two triplets at δ 88.24 and 85.36 respectively (J = 20 Hz). In addition to these, signals corresponding to the recently reported $[Mo\{P(CH_2CH_2PPh_2)_3\}_2]$[19] also appear, **C**. The stability of this complex may indicate that its formation is a feasible decomposition pathway for the dinitrogen complex, at least for one possible isomer. The two triplets in the $^{31}P-\{^1H\}$ NMR spectrum suggest an A_2M_2 spin system, and if we consider that there is no coupling between the central phosphorus atom of the ligand and the non-co-ordinated ones the structures **E** and **F** would be in agreement with such a pattern, whereas **D** should generate an AA′MM′ pattern which cannot be disregarded, although it would implicate the same value for $(^2J_{PP})_{cis}$ and $(^2J_{PP})_{trans}$, which seems unlikely. Substitution of dinitrogen in this isomer by the pendant phosphorus atoms would produce **C**. Both **E** and **F** would account for the observed A_2M_2 pattern. However, **F** implicates a *cis* arrangement for the dinitrogen ligands, which is not in agreement with the presence of only one ν(N≡N) band in the IR spectrum, unless the two bands corresponding to a *cis*-bis(dinitrogen) are accidentally degenerate. This fact has not been reported for any known *cis*-bis(dinitrogen) complex, as far as we are aware. Therefore, structure **E** seems to be the most reasonable tentative assignment for **6**.



G

Substitution Reaction of cis-$[Mo(N_2)_2(PMe_3)_4]$ *with* $N(CH_2CH_2PPh_2)_3$.—An attempt has been made to use a different way to prepare a dinitrogen complex of molybdenum(0) with $N(CH_2CH_2PPh_2)_3$ as coligand. We studied the substitution reaction of the complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with $N(CH_2CH_2PPh_2)_3$ in thf at 40–50 °C during a period of 48 h. After this treatment dark red crystals were obtained. This product is soluble in thf and benzene and shows low solubility in light petroleum and diethyl ether. Its elemental microanalysis is in agreement with the formula $[Mo(N_2)(PMe_3)\{N(CH_2CH_2PPh_2)_3\}]$ **7**. In the IR spectrum the compound shows a band at 1925 cm^{-1} in the region of $\nu(N{\equiv}N)$ stretching, which is suggestive of a mono(dinitrogen) compound. In addition, the characteristic frequencies corresponding to the $N(CH_2CH_2PPh_2)_3$ ligand (1000–1200 cm^{-1}) and an intense band at 950 cm^{-1} corresponding to the PMe_3 ligand are observed. The ^{31}P-$\{^1H\}$ NMR spectrum in benzene in the region δ 50–60 is very similar to that of **1** except for the more complex coupling due to the presence of co-ordinated trimethylphosphine. A multiplet is observed at δ 57.35 corresponding to two equivalent phosphorus atoms in $N(CH_2CH_2PPh_2)_3$ (**1** shows a doublet in approximately the same position) and another multiplet at δ 51.5 (**1** shows a triplet in the same region) for the remaining P coupled with the previous two phosphorus atoms and to the phosphorus in PMe_3. A multiplet at δ 8.83 is observed corresponding to phosphorus in PMe_3 coupled with the P atoms of $N(CH_2CH_2PPh_2)_3$. All these data allow us to propose a structure **G** for **7**.

This compound is obtained only by heating and after 48 h of reaction, possibly due to the relatively high stability of *cis*-$(Mo(N_2)_2(PMe_3)_4]$, and therefore difficulty in phosphine-replacement reactions in this complex.

Conclusion

Three dinitrogen complexes of molybdenum with the tripodal ligands $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$ have been isolated. Two are bis(dinitrogen) complexes, **1** and **6**, which have been prepared by reduction of the corresponding precursor $[MoCl_3L]$ [L = $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$], and are relatively unstable, losing dinitrogen in a few days at room temperature. By substitution of trimethylphosphine and N_2 from *cis*-$[Mo(N_2)_2(PMe_3)_4]$, complex **7** has also been obtained. The chemical reactivity of **1** towards CO, PMe, MeI and CF_3CO_2H has been studied. The reactions with CO and PMe_3 yielded **2** and **3** respectively. The protonation of the dinitrogen complex with CF_3CO_2H failed, and **5** was obtained. In a similar fashion, reaction with MeI only yielded the oxidized derivative **4**.

Experimental

All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen.[20] All solvents were distilled from appropriate drying agents immediately prior to use.

The ligand tris(2-diphenylphosphinoethyl)amine was synthesised according to a literature procedure[21] by reaction between $KPPh_2{\cdot}2C_4H_8O_2$[22] and $N(CH_2CH_2Cl)_3$.[23] The precursor complexes $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ and $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]$ were prepared as we have recently reported.[5] The complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ was synthesised as described in ref. 24. All the other reagents were commercially available, and were used without further purification.

Microanalytical data were obtained by Mr. Colin MacDonald, AFRC-IPSR NFL, University of Sussex, or by Butterworth Laboratories. Ammonia and hydrazine were determined spectrophotometrically using the indophenol[25] and *p*-dimethylaminobenzaldehyde[26] methods respectively. Infrared spectra were recorded on a Philips Analytical SP3-300 spectrophotometer using either Nujol mulls or KBr pellets, ^{31}P-$\{^1H\}$ NMR spectra on a Varian XL-200 spectrometer using thf with a C_6D_6 capillary inside the NMR tube, to provide lock signal, unless otherwise stated, and 85% H_3PO_4 as reference.

cis-$[Mo(N_2)_2\{N(CH_2CH_2PPh_2)_3\}]$ **1**.—A suspension in thf (50 cm^3) of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ (1.28 g, 1.5 mmol) was added to a sodium dispersion (1 g of a 40% dispersion in mineral oil) in a flask cooled in an ice–salt bath and stirred for 1 h at 0 °C. Then it was stirred for 4 h at room temperature, giving a dark orange suspension, which was centrifuged. The dark orange solution was kept for 15 h at −20 °C, yielding a microcrystalline, bright orange solid. This was filtered off, washed with light petroleum (b.p. 60–70 °C) and dried under a dinitrogen stream. Yield 0.5 g, 45% (Found: C, 62.8; H, 5.20; N, 8.1. $C_{42}H_{42}MoN_5P_3$ requires C, 62.6; H, 5.20; N, 8.7%). IR (Nujol mull): 1970, 1898, 1590, 1570, 1180, 1100, 1070, 750 and 690 cm^{-1}. ^{31}P-$\{^1H\}$ NMR: δ 55.15 (d, 2P) and 50.28 (t, 1P), J(P–P) = 12.8 Hz.

fac-$[Mo(CO)_3\{N(CH_2CH_2PPh_2)_3\}]$ **2**.—A suspension of complex **1** (1 g, 1.19 mmol) in thf (50 cm^3) was treated with CO at 1 atm. After 15 h a yellow solution was obtained. This was concentrated under vacuum and left undisturbed for several hours at −20 °C, yielding a yellow solid which was filtered off, washed with light petroleum and dried *in vacuo*. The product was recrystallized from acetone as yellow needles. Yield 0.7 g, 80% (Found: C, 64.9; H, 5.05; N, 1.55. $C_{45}H_{42}MoNO_3P_3$ requires C, 64.8; H, 5.05; N, 1.70%). IR (Nujol mull): 1950, 1840, 1590, 1180, 1100, 1060, 750 and 690 cm^{-1}. ^{31}P-$\{^1H\}$ NMR: δ 60 (s).

$[Mo(PMe_3)_3\{N(CH_2CH_2PPh_2)_3\}]$ **3**.—To a suspension of complex **1** (1 g, 1.19 mmol) in thf (50 cm^3) was added an excess (*ca.* 7:1 mol equivalents) of PMe_3. The mixture was stirred overnight with formation of a microcrystalline dark orange solid. This product was washed with light petroleum and dried *in vacuo*. Yield 0.7 g, 60% (Found: C, 62.6; H, 7.05; N, 1.40. $C_{51}H_{69}MoNP_6$ requires C, 62.6; H, 7.05; N, 1.45%). IR (Nujol mull): 1590, 1570, 1180, 1100, 950, 750, 740 and 690 cm^{-1}.

$[MoI_2\{N(CH_2CH_2PPh_2)_3\}]$ **4**.—A suspension of **1** (1 g, 1.19 mmol) in benzene (50 cm^3) was cooled to the temperature of boiling dinitrogen and treated with an excess of MeI (1 cm^3). The reaction mixture was slowly warmed to room temperature and then stirred overnight. An orange suspension was obtained from which a yellow-orange solid was recovered. It was washed with light petroleum and dried *in vacuo*. Yield 0.48 g, 40% (Found: C, 49.9; H, 4.35; N, 1.40. $C_{42}H_{42}I_2MoNP_3$ requires C, 50.3; H, 4.20; N, 1.40%). IR (Nujol mull): 1590, 1570, 1100, 750, 740 and 690 cm^{-1}.

$[Mo(CF_3CO_2)_2\{N(CH_2CH_2PPh_2)_3\}]$ **5**.—To a suspension of complex **1** (1 g, 1.19 mmol) in thf (50 cm^3) was added CF_3CO_2H (1.1 cm^3, 1.19 mmol). The reaction flask was immersed in an ethanol–liquid dinitrogen bath for 1 h. Then the reaction mixture was stirred for 3 h at room temperature. The orange solid which formed was filtered off, washed with light petroleum and dried *in vacuo* (from the solution cooled at −20 °C overnight more product was recovered). Yield 1.3 g, 70% (Found: C, 57.4; H, 4.70; N, 1.55. $C_{46}H_{42}F_6MoNO_4P_3$ requires C, 56.6; H, 4.30; N, 1.45%). IR (KBr pellets): 3010, 2960, 2800, 1680–1650, 1200–1110, 1100, 1080, 750 and 690 cm^{-1}.

trans-[Mo(N_2)$_2${P($CH_2CH_2PPh_2$)$_3$}$_2$] **6**.—This compound was obtained as an orange solid following a method similar to that used in the preparation of **1**, starting from [MoCl$_3$-{P($CH_2CH_2PPh_2$)$_3$}] (1.3 g, 1.5 mmol). Yield 0.7 g, 30% (Found: C, 66.85; H, 6.05; N, 1.90. $C_{84}H_{84}MoN_4P_8$ requires C, 67.55; H, 5.6; N, 3.75%). IR (Nujol mull): 1950, 1590, 1150, 1125, 1095, 750, 740 and 680 cm^{-1}. ^{31}P-{^{1}H} NMR: δ −11.5 (m, 4P), 85.36 (t, 2P) and 88.24 (t, 2P); *J*(P–P) = 20 Hz.

cis-[Mo(N_2)(PMe_3){N($CH_2CH_2PPh_2$)$_3$}] **7**.—To a solution of *cis*-[Mo(N_2)$_2$(PMe_3)$_4$] (1.32 g, 3.0 mmol) in thf (50 cm^3) was added N($CH_2CH_2PPh_2$)$_3$ (1.9 g, 3.0 mmol). The resulting dark orange solution was stirred for 15 h. The solvent was removed *in vacuo* and the residue treated with benzene (30 cm^3). After centrifugation the solution was concentrated *in vacuo* and left undisturbed for several days at room temperature. A microcrystalline red-brown solid was obtained. Yield 1.02 g, 40% (Found: C, 63.6; H, 6.35; N, 3.90; P, 14.1. $C_{45}H_{51}MoN_3P_4$ requires C, 63.3; H, 6.00; N, 4.90; P, 14.5%). IR (Nujol mull): 1925, 1580, 1570, 1180, 1100, 1095, 950, 750, 740, 690 and 680 cm^{-1}. ^{31}P-{^{1}H} NMR (C_6D_6): δ 8.83 (m, 1P), 51.5 (m, 1P) and 57.35 (m, 2P).

Acknowledgements

We are grateful for financial support from Dirección General de Investigación Cientifica y Técnica (Proyecto PB88-0413) and from the Junta de Andalucía. We also thank Professor E. Carmona (Universidad de Sevilla) for allowing access to the facilities used to obtain NMR data and Mr. Colin MacDonald, at the AFRC-IPSR Nitrogen Fixation Laboratory, for the microanalysis.

References

1 R. A. Henderson, G. J. Leigh and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **23**, 197.
2 C. Bianchini, M. Dante, A. Meli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, 1988, **110**, 6411.
3 F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1992, 33.
4 L. Sacconi and F. Mani, *Transition Metal Chemistry*, eds. G. A. Melson and B. N. Figgis, Marcel Decker, New York, 1982, vol. 8, p. 179.
5 M. J. Fernández-Trujillo, M. García Basallote, P. Valerga, M. C. Puerta and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1991, 3149.
6 E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood and R. D. Rogers, *Polyhedron*, 1983, **2**, 185.
7 T. A. George and R. C. Tisdale, *Inorg. Chem.*, 1988, **27**, 2909.
8 T. A. George and R. A. Kovar, *Inorg. Chem.*, 1981, **20**, 285.
9 J. Chatt, A. J. Pearman and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 2139.
10 N. J. Lazarowych, R. H. Morris and J. M. Ressner, *Inorg. Chem.*, 1986, **25**, 3926.
11 B. B. Kaul, R. K. Hayes and T. A. George, *J. Am. Chem. Soc.*, 1990, **112**, 2002.
12 E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood, R. D. Rogers and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 441.
13 T. A. George and C. D. Seibold, *Inorg. Chem.*, 1973, **12**, 2548.
14 M. Brookhart, K. Cox, F. Geoffrey, N. Cloke, J. C. Green, M. L. H. Green, P. M. Hare, J. Bashkin, A. E. Derome and P. D. Grebenik, *J. Chem. Soc., Dalton Trans.*, 1985, 423.
15 C. A. Ghilardi, P. Innocenti, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1986, 2075.
16 C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci and A. Traversi, *J. Chem. Soc., Dalton Trans.*, 1990, 2293.
17 D. C. Busby, T. A. George, S. D. Allen Iske, jun. and S. D. Wagner, *Inorg. Chem.*, 1981, **20**, 22.
18 T. A. George, Lindun Ma, S. M. Shailh, R. C. Tisdale and J. Zubieta, *Inorg. Chem.*, 1990, **29**, 4789.
19 M. García Basallote, P. Valerga, M. C. Puerta Vizcaíno, A. Romero, A. Vegas and M. Martínez Ripoll, *J. Organomet. Chem.*, 1991, **420**, 371.
20 D. F. Shriver, *Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969.
21 R. Morasi and L. Sacconi, *Inorg. Synth.*, 1976, **16**, 173.
22 K. Issleib and A. Tzschach, *Chem. Ber.*, 1959, **92**, 1118.
23 J. P. Mason and D. J. Gasch, *J. Am. Chem. Soc.*, 1938, **60**, 2816.
24 E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Am. Chem. Soc.*, 1983, **105**, 3014.
25 M. W. Weatherburn, *Anal. Chem.*, 1967, **39**, 971.
26 G. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006.

Received 16*th September* 1992; *Paper* 2/04573B