

Polypyrazolylborate analogues without boron: Structural diversity in ligand design and metal complexes

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Abstract. Structural chemistry of organometallic complexes containing pyrazole-derived polydentate ligands (without boron) has been reviewed in the context of current results from this laboratory.

Keywords. Organometallic; pyrazolyl; structure; stereochemistry.

1. Introduction

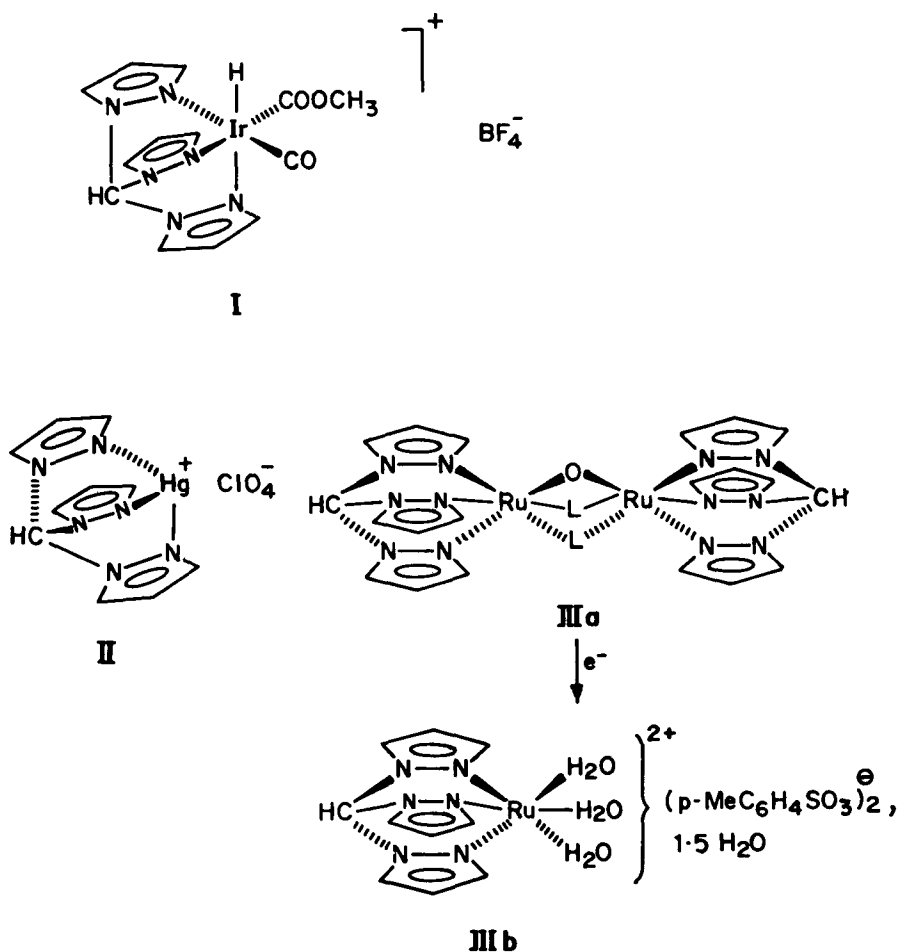
The chemistry of pyrazole-derived ligands was initiated by Trofimenko and has been extensively reviewed by him (Trofimenko 1986, 1993). Although initially developed as an isoelectronic alternative to the ubiquitous cyclopentadienyl ligand, it was soon realised that the pyrazole-derived ligands have a rich chemistry of their own. In particular, three ligands have markedly different stereoelectronic requirements compared to the conventional pyridine or phosphine-derived ligands. Therefore, the structures and reactivities of metal complexes containing pyrazole-derived polydentate ligands varied widely from previously known analogues.

Over the years, the ligand modifications concerned variation of ring size of the chelates and substituents on the pyrazole. Such changes allowed fine tuning of steric and/or electronic influences on the metal centres. The following discussion provides an overview of this general trend from current literature. The polypyrazolylborates have been excluded in view of a recent review (Trofimenko 1993), and the literature was scanned from 1986 for the various other pyrazole-derived ligands since earlier reports were already reviewed (Trofimenko 1986).

Trofimenko described (Trofimenko 1970) the preparation of polypyrazolylmethanes and some of their ligation properties. The *tris*-pyrazolylmethane derivatives can be regarded as the neutral analogue of the uninegative *tris*-pyrazolylborates. The olefin-complexes of rhodium and iridium were characterised (Esteruelas *et al* 1988) and formation of alkoxycarbonyl derivatives (I) were later reported (Esteruelas *et al* 1989).

Moderately stable derivatives were prepared from zinc (Lobbia *et al* 1987), cadmium (Lobbia *et al* 1987) and mercury (Lobbia *et al* 1989) (II), and characterised by IR and NMR spectroscopy. Structurally characterised mononuclear aquo complex (Llobet *et al* 1990) as well as the ones containing bipyridyl ligand (Llobet and Doppeit 1988) were reported for ruthenium. A bridged diruthenium complex (III) was also prepared

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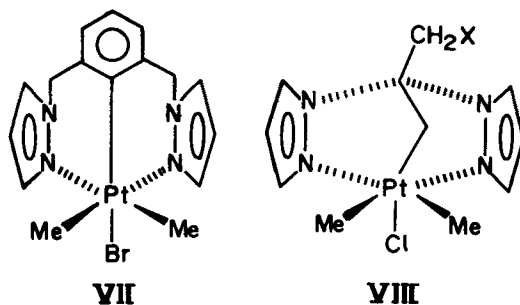
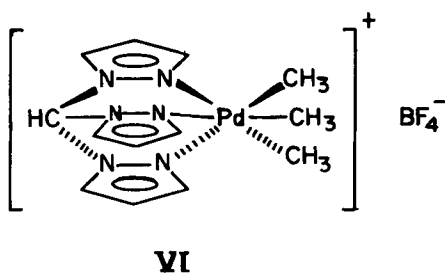
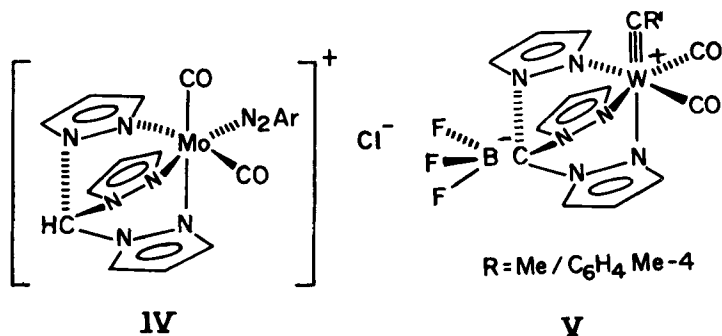


(Llobet *et al* 1989). Upon reduction of this dimeric species, the mononuclear *tris(aquo)* complex was obtained quantitatively.

While an interesting molybdenum diazonium complex could be prepared using the tridentate *tris-pyrazolylmethane* ligand (Deane *et al* 1990), a number of Mo and W alkylidyne complexes were reported by Angelia (Doyle and Angelia 1989) and Stone (Byers and Stone 1990). The first isolable complex (VI) of Pd(IV) featured this tridentate ligand (Byers *et al* 1987, 1990; Brown *et al* 1990).

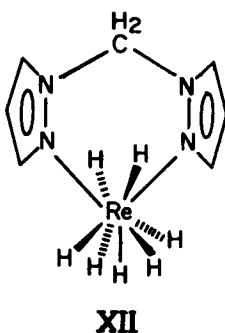
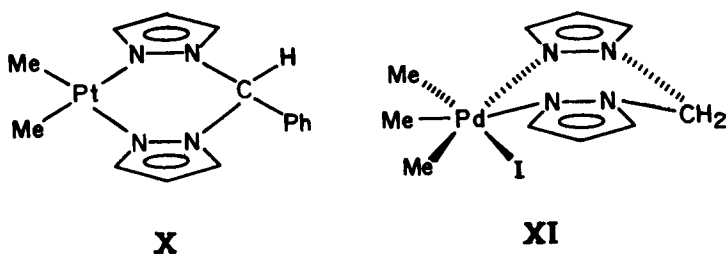
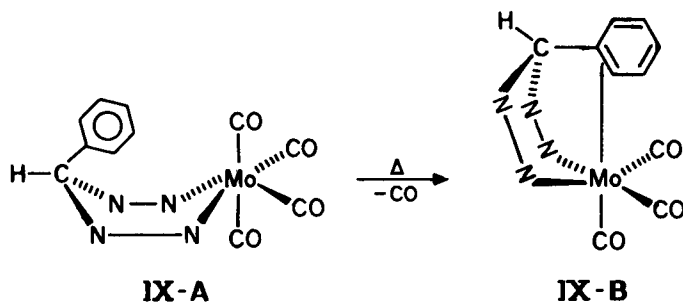
Intramolecular oxidative addition of R-X on suitably designed substrate was also possible (Canty *et al* 1990), as shown in (VII) and (VIII) (Canty *et al* 1986). Palladium complexes were also prepared with a structurally related mixed ligand where one pyrazole was replaced by a pyridine (Byers *et al* 1990).

The chemistry of bidentate *bis-pyrazolylmethane* derivatives has also been investigated by several groups. A number of complexes are known with zinc (Leonesi *et al* 1987), cadmium (Leonesi *et al* 1987), mercury (Lorenzotti *et al* 1985; Cingolani *et al* 1987) and tin (Visalakshi *et al* 1986, 1989; Lobbia *et al* 1987). Solution behaviour and



X-ray structure of silver complexes have been studied (Lorenzotti *et al* 1990). The stoichiometry of metal:ligand is 1:1 in most of the complexes with the exception of some complexes of mercury and silver.

While a copper(I) complex featuring this bidentate ligand was prepared and characterised (Bonati *et al* 1990), a great deal of activity centred around molybdenum and tungsten complexes. The $M(\text{CO})_4$ derivatives were prepared (Shiu and Chang 1987; Shiu and Liou 1988; Lobbia and Bonati 1989) and converted to M(II) dihalides (Shiu *et al* 1989, 1990) or π -allyl complexes (Shiu and Chang 1987; Shiu and Liou 1988). An unusual η^2 -arene complex (IX) was structurally characterised by X-ray crystallography (Shiu *et al* 1990) when the bridging carbon was linked with a phenyl ring.



A number of complexes were prepared from palladium(II) and platinum(II) metal centres (Byers and Canty 1985, 1990; Minghetti *et al* 1986; Canty and Honeyman 1990) as well as those metals in IV state (Visalakshi & Jain 1990; Byers *et al* 1990). Some of the latter complexes were reported to be fluxional (X) and (XI) (Byers *et al* 1990). Formation of heterobimetallic complexes of palladium and platinum with the *bis*-pyrazolyl-methane ligand as bridged, has been reported (Clerk *et al* 1986). Crabtree (Hamilton *et al* 1989) reported the first transition metal polyhydride complex featuring this bidentate ligand (XII). Ligands have been synthesised where nitrogen was retained as the capping atom of *bis* or *tris*-pyrazolyl derivatives. In most instances, the capping nitrogen took part in complexation through its lone pair.

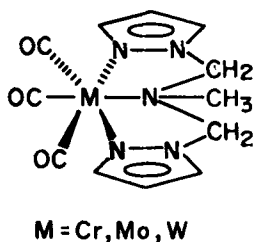
Shiu (Shiu and Vong 1987; Shiu *et al* 1989) investigated several molybdenum and tungsten complexes of structures (XIII) and (XIV).

The π -allyl complex was shown to be fluxional and the dynamic structure was believed to have resulted from a *trigonal twist* involving the tridentate ligand. In the X-ray structure it was observed that the capping nitrogen as well as one pyrazole occupied positions *trans* to the CO ligands.

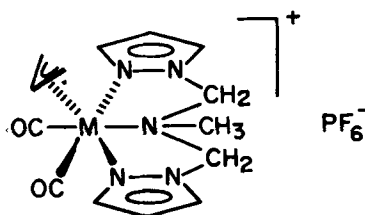
A large number of copper complexes were prepared and characterised using ligands derived from pyrazoles, a capping nitrogen atom and variable spacer connection between the capping nitrogen and the pyrazoles. Among the complexes derived from the ligand *N,N*-bis(3,5-dimethyl-1-pyrazolylmethyl) aminoethane (Pennings *et al* 1988), a tridentate ligand environment was characterised by X-ray crystallography (XV) (Pennings *et al* 1988).

Dimeric complexes of cobalt, copper, nickel and zinc with this ligand were reported (XVI) (Van Driel *et al* 1985; Kleywegt *et al* 1985; Vildhuis *et al* 1986). Hexacoordinated and pentacoordinated structures have been characterised (XVII) (Driessen *et al* 1988).

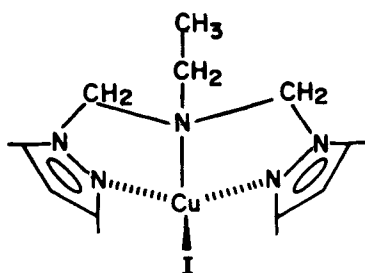
Another form of ligands featuring two pyrazoles in conjunction with a phenolate ion and copper complexes was investigated (Sorrel *et al* 1986, 1987; Di Vaira and Mani 1985; Driessen *et al* 1987) in the context of bioinorganic interests. Examples of these and related complexes (Reibenspies *et al* 1987) follow (XVIII), (XIX) and (XX). Various other ligands (Addison *et al* 1988; Paap *et al* 1988; Haanstra *et al* 1989, 1990) were studied where pyrazoles were used as mixed donor sites with nitrogen and sulphur.



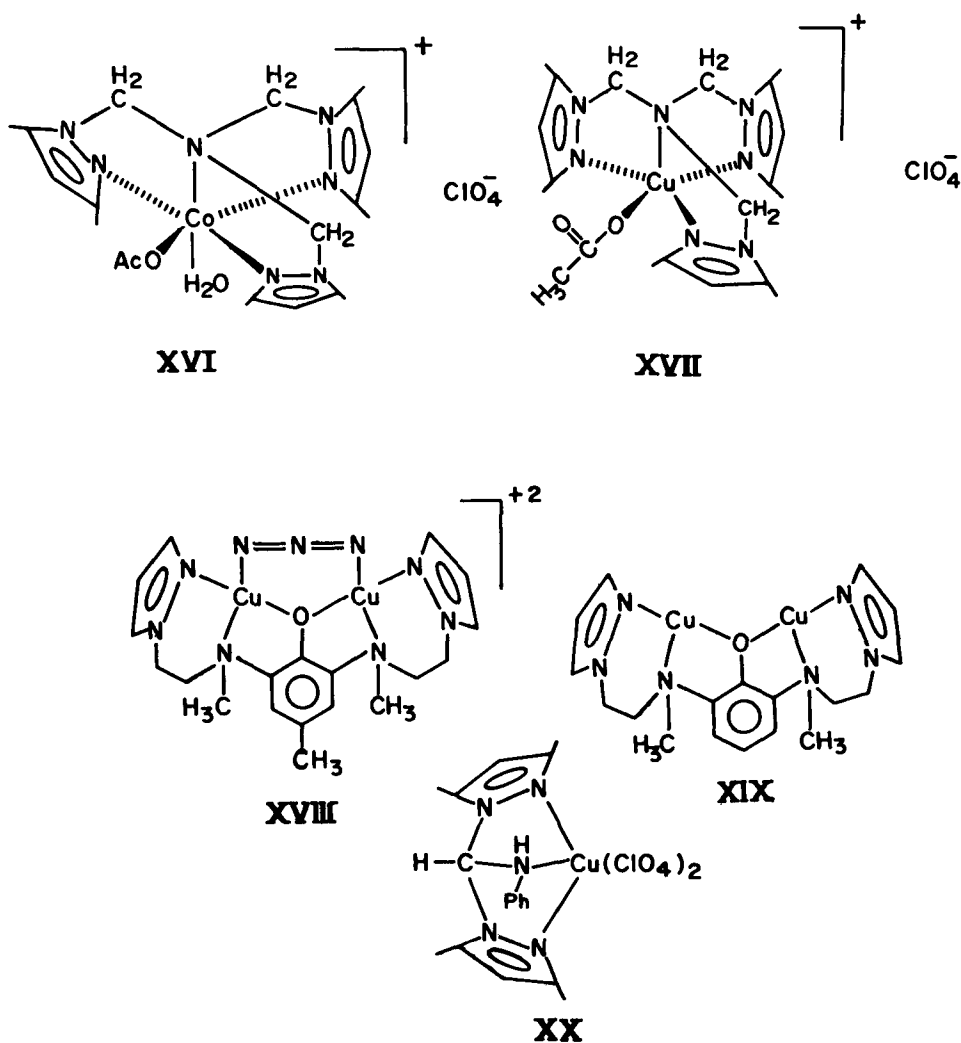
XIII



XIV



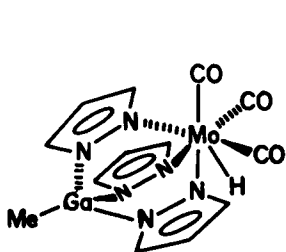
XV



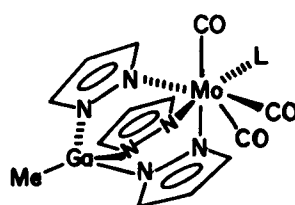
A large number of complexes were prepared with ligands derived from pyrazoles and gallium as the capping atom. *Tris*-pyrazolygallates have been used in different complexes ranging from monomeric (Onyiriuka and Storr 1987) to heterobimetallic with direct (Onyiriuka *et al* 1986) or bridging linkages (XXI), (XXII), (XXIII) and (XXIV) (Banta *et al* 1986).

The other aspects of the gallium derived ligands (Chong *et al* 1990; Rettig *et al* 1988; Gracey *et al* 1987; Onyiriuka and Storr 1987; Copper *et al* 1986; Louie *et al* 1985, 1985; Nussbaum and Storr 1985) concern complexes like XXV and XXVI. The unsymmetrical ligand environment generated interesting stereochemical features and occasionally resulted in fluxional structures.

As with gallium, if a metal atom could be used as capping atom in such pyrazole-bridged complexes, the bimetallic species would be interesting both from the consideration

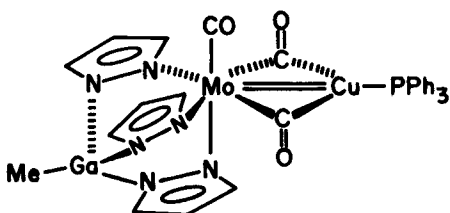


XXI

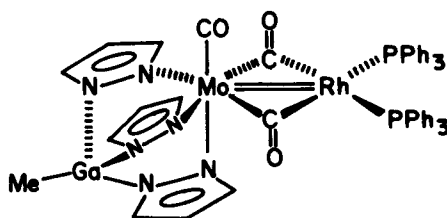


L = Ph₃Sn, Me₃Sn, Me₂ClSn

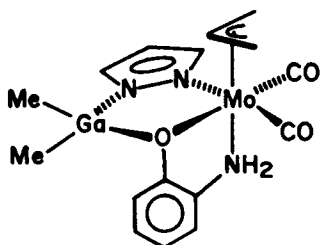
XXII



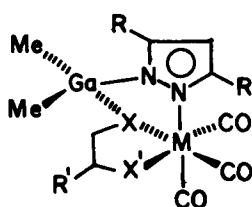
XXIII



XXIV

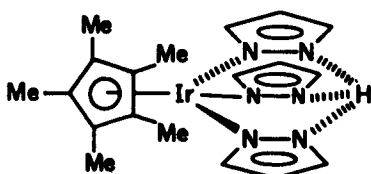


XXV

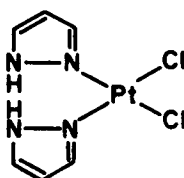


XXVI

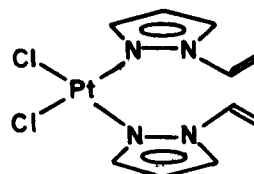
M = Mn, Re
 R = H, Me
 R = H, Me, Et
 X = O, S
 X' = NH₂, NMe₂, SPh, SEt.



XXVII



XXVIII



XXIX

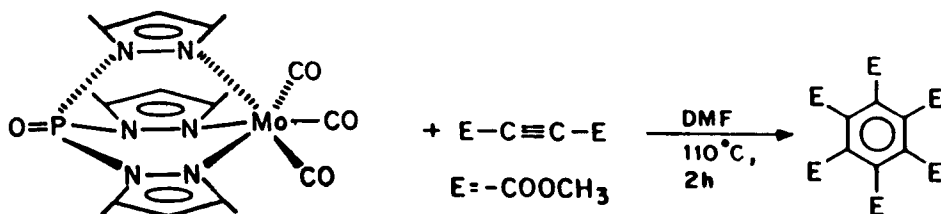
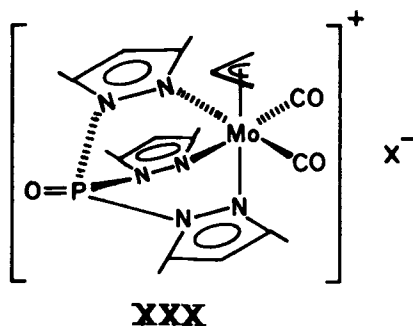
of reactivity and as potential precursors for material applications. Progress in this direction awaits future endeavours. However, certain related structures (Carmona *et al* 1986; Cinellu *et al* 1989; Voropaev *et al* 1986; Liu *et al* 1985) should be noted. The last three structures represent potential ligands for heterobimetallic complexes (XXVII), (XXVIII) and (XXIX).

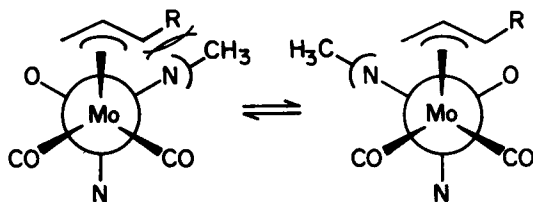
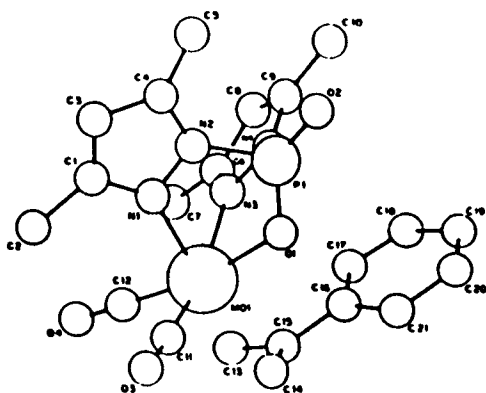
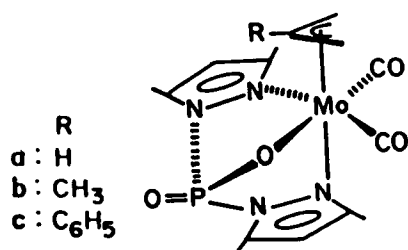
We were interested in developing a new ligand system derived from pyrazole, which would provide a set of structurally defined, mononuclear complexes that would be relatively air-stable, and which can be directly utilised in useful, organic transformations. Molybdenum(II) π -allyl complex was chosen as the parent structural unit, and *tris*(3,5-dimethyl-1-pyrazolyl) phosphine oxide was selected as a symmetrical, six-electron donor, tridentate ligand. The combination was expected to provide a cationic complex (XXX) which should readily undergo nucleophilic attack at the π -allyl site.

The proposed ligand was reported in the literature (Fischer *et al* 1976), but no metal complex was reported with this compound. The preparative procedure was modified for simplicity of operation (the purified ligand could be stored in the refrigerator under pet ether for months), and complexation with molybdenum hexacarbonyl was examined.

Thermal displacement of three CO ligands from $\text{Mo}(\text{CO})_6$ by the tridentate ligand resulted in a sparingly soluble, symmetrical complex, Reaction of this complex (XXXI) with three equivalents of dimethyl acetylenedicarboxylate in refluxing DMF did not produce the desired acetylene complex, but resulted in the formation of hexacarbomethoxybenzene as the major product (40% yield). Such acetylene trimerisation is seldom reported for $\text{Mo}(\text{O})$ complexes.

The first set of π -allyl complexes were synthesised by refluxing $\text{Mo}(\text{CO})_6$ in acetonitrile with allyl halides for several hours followed by addition of the ligand. The

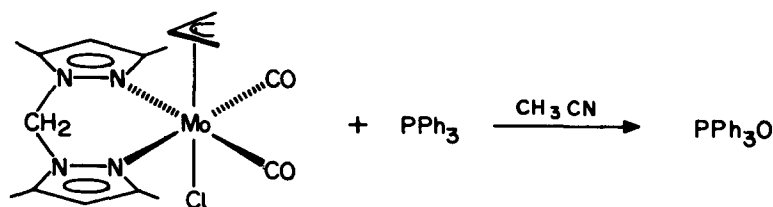




proton NMR spectra of these complexes revealed the presence of two pyrazoles rather than three, and the X-ray structure of a complex confirmed the replacement of one pyrazole unit by an oxygen atom. The origin of this oxygen atom in the complex is yet unclear (Joshi *et al* 1991).

These complexes were stereochemically non-rigid and exhibited considerable line-broadening in the proton NMR spectra at room temperature. On cooling, the peaks decoalesced and sharpened, and the only conformer present could be readily identified. We did not observe any trace of the conformer where the oxygen atom resided *trans* to the allyl group. A preliminary EHMO calculation supported the observation.

The proximity of a terminal allyl substituent and the 3-methyl group of the pyrazole, and consequent steric effects were probed in a series of isostructural complexes. The



results showed that weak interactions such as a CH/ π attraction, can dictate conformational preferences in these complexes (Chowdhury *et al* 1994).

For a severely hindered tripyrazolylborate system, a distortion of the *n*-allyl orientation may result (Joshi *et al* 1995).

Molybdenum π -allyl complexes containing bis(3,5-dimethylpyrazolyl)methane ligand are unexceptional in terms of structure (Joshi *et al* 1991) but they were readily converted to a dimeric Mo(V) oxo complex on exposure to air. As a rare occurrence, such Mo(II) precursors were capable of activating dioxygen and transferring oxygen to triphenylphosphine catalytically (Joshi *et al* 1993). The scope and mechanism of this reaction is being investigated.

In summary, pyrazole-derived metal chelates display a varied and fascinating chemistry – both in terms of structural diversity and unusual reactivity – which will be explored extensively in the coming decades.

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