

## Synthesis and Crystallographic Characterization of Bis(tetracarbonylphenyldiazomanganese), a Unique Complex with Bridging Aryldiazo-ligands

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**Summary** The reaction of trimethylsilylphenyldi-imine and bromopentacarbonylmanganese provided bis(tetracarbonylphenyldiazomanganese); the molecular structure has been determined crystallographically, and has been shown to contain the previously unreported bridging phenyldiazo-group.

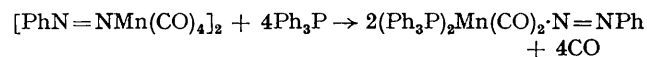
A NUMBER of aryldiazo-derivatives of transition metals has been reported, from reactions of diazonium salts and phenylhydrazine.<sup>1,2</sup> In these compounds the aryldiazo-ligand behaves as a formally three-electron donor to one metal atom.<sup>3</sup>

Whilst diazonium salts are reported<sup>1</sup> not to react with the pentacarbonylmanganese anion to form aryldiazomanganese derivatives, we obtained the stable bis(tetracarbonylphenyldiazomanganese) from an alternative reagent. Organosilicon and organotin bases have previously been shown to be useful routes for the formation of many novel inorganic complexes,<sup>4</sup> and we now note the use of trimethyl-

silylphenyldi-imine.<sup>5</sup> This reacts with bromopentacarbonylmanganese (25°; 6 days) possibly by an initial displacement of carbon monoxide, followed by elimination of bromotrimethylsilane.

The product is dimeric, and is unique in that the phenyldiazo-ligand acts as a three-electron donor by bridging two metal atoms.

There appears, however, to be a delicate balance between bridging and terminal phenyldiazo-ligands on manganese, since triphenylphosphine displaces carbon monoxide with concomitant bridge fission. The five-co-ordinate product is mononuclear, isoelectronic<sup>6</sup> with  $[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\cdot\text{N}=\text{NPh}]^+$ , and the phenyldiazo-ligand has reverted to a terminal formally three-electron donor role.

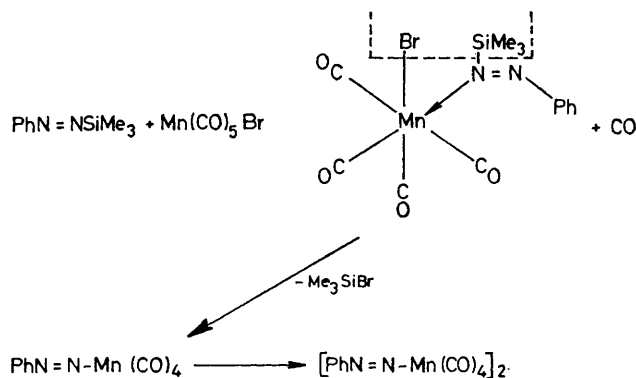


The molecular geometry of  $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$  has been determined unambiguously *via* a single-crystal X-ray diffraction study.

**Crystal data:**  $\text{C}_{20}\text{H}_{10}\text{Mn}_2\text{O}_8$ ,  $M = 544.2$ , triclinic, space group  $P\bar{1}[C_1; \text{No. } 2]$ . Cell dimensions (at 23.5°C) are  $a = 7.2358(13)$ ,  $b = 8.8893(17)$ ,  $c = 9.4677(18)$  Å,  $\alpha = 80.52(2)^\circ$ ,  $\beta = 77.38(1)^\circ$ ,  $\gamma = 71.44(1)^\circ$ ,  $U = 560.4$  Å<sup>3</sup>,  $D_m = 1.59(2)$ ,  $D_c = 1.613$ ,  $Z = 1$ ,  $\mu$  (Mo- $K_\alpha$ ) = 12.5 cm<sup>-1</sup>.

Diffraction data were collected with a Picker FACS-1 automated diffractometer and the structure was solved by Patterson, Fourier, and least-squares techniques. All atoms (including hydrogens) were located. The final  $R$ -value is 3.43% for the 1974 reflections which represent data complete to  $2\theta = 50^\circ$  (Mo- $K_\alpha$  radiation).

The molecular geometry is shown in the Figure. The molecule lies at a crystallographic centre of symmetry; the two  $\text{Mn}(\text{CO})_4$  units are linked together by two bridging



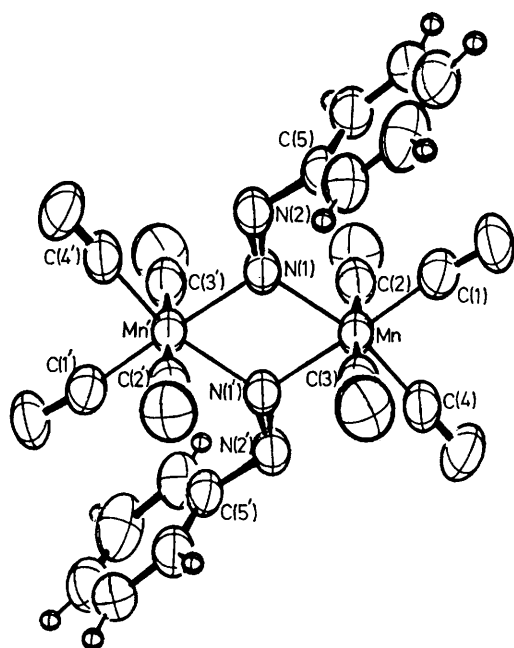


FIGURE. Molecular geometry of  $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ .

phenyldiazo-ligands, with  $\text{Mn}-\text{N}(1) = \text{Mn}'-\text{N}(1') = 2.031(2)$  Å and  $\text{Mn}-\text{N}(1') = \text{Mn}'-\text{N}(1) = 2.021(2)$  Å. The  $\text{Mn} \cdots \text{Mn}'$  distance of  $3.234(1)$  Å is non-bonding, as is evidenced by the angles within the strictly planar  $\text{Mn}_2\text{N}_2$  core of the molecule, *viz.*,  $\text{Mn}-\text{N}(1)-\text{Mn}' = \text{Mn}'-\text{N}(1')-\text{Mn} = 105.9(1)^\circ$  and  $\text{N}(1)-\text{Mn}-\text{N}(1') = \text{N}(1')-\text{Mn}'-\text{N}(1) = 74.1(1)^\circ$ . The  $\text{N}(1)-\text{N}(2)$  distance of  $1.234(3)$  Å within the phenyldiazo-group is consistent with its formulation as  $\text{N}=\text{N}$ . The  $\text{N}(2)-\text{C}(5)$  bond length is  $1.445(3)$  Å, while the angle  $\text{N}(1)-\text{N}(2)-\text{C}(5)$  is  $119.7(2)^\circ$ .

The geometry about  $\text{N}(1)$  is irregular, with  $\angle \text{Mn}-\text{N}(1)-\text{N}(2) = 134.4(2)^\circ$  as opposed to  $\angle \text{Mn}'-\text{N}(1)-\text{N}(2) = 119.6(2)^\circ$ . This apparently results from the steric interaction of the phenyl group with an equatorial carbonyl ligand, since  $\angle \text{N}(1)-\text{Mn}-\text{C}(1) = 103.4(1)^\circ$  a value some  $10^\circ$  larger than the  $93.5(1)^\circ$  found for  $\angle \text{N}(1')-\text{Mn}-\text{C}(4)$ . The contact  $\text{C}(1) \cdots \text{C}(5)$  is only  $2.973(3)$  Å.

Distances and angles in the carbonyl ligands are normal, with  $\text{Mn}-\text{C}(\text{equatorial}) = 1.836(3)$  and  $1.845(3)$  Å,  $\text{Mn}-\text{C}(\text{axial}) = 1.858(4)$  and  $1.869(4)$  Å, and  $\text{C}-\text{O} = 1.128(4)-1.139(3)$  Å.

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