Reactions of Nitrosoarenes with the Molybdenum–Molybdenum Triple Bond

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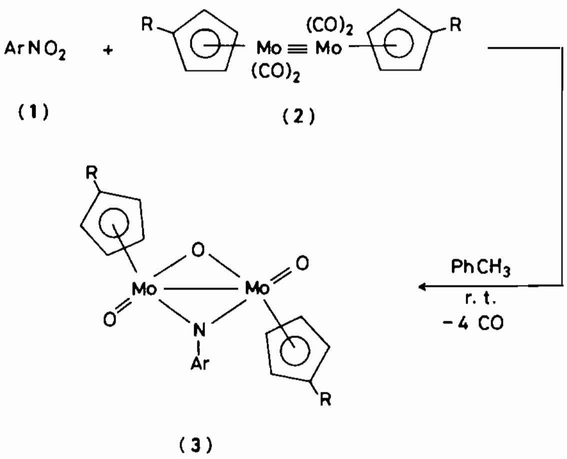
Recently we described the novel reaction of nitroarenes (*1*) with cyclopentadienylmolybdenum dicarbonyl dimer (*2*, R = H) and related complexes containing a metal–metal triple bond. The products of these reactions are complexes (*3*) having bridging and terminal oxygen ligands. These complexes result from complete decarbonylation of *2* [1].



It seemed conceivable to us that the reaction may proceed *via* initial deoxygenation of the nitro compound to a nitrosoarene. If correct, then nitrosobenzenes should react with *2* to afford the same class of complexes. We now report the realization of this process.

Treatment of nitrosobenzene and *o*-nitrosotoluene with *2*, R = H in toluene at room temperature afforded *3*, R = H. The same type of complex was obtained using the methylcyclopentadienyl complex *2*, R = CH_3, as the reactant. Azobenzenes (*4*) were byproducts of these reactions. The complexes (*3*) obtained from nitrosobenzenes gave the same characteristic infrared and nuclear magnetic resonance spectra (Table I) as those previously prepared from nitroarenes [1].

$$3ArNO + 2 \xrightarrow[r.t.]{PhCH_3} 3 + \underset{(4)}{ArN = NAr}$$

In conclusion, nitrosobenzenes may be intermediates in the conversion of nitro compounds to the binuclear molybdenum oxo complexes (*3*).

Acknowledgement

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References

1 H. Alper, J. F. Petrignani, F. W. B. Einstein and A. C. Willis, *J. Am. Chem. Soc., 105*, 1701 (1983).

TABLE I. Spectral Properties of *3*[a].

2, R =	ArNO	IR[b] $\nu_{Mo=O}$ cm^{-1}	ν_{Mo-O}	NMR[c] δ ppm
H	PhNO	898	815	6.03(s, 10H, C_5H_5) 7.10–7.90(m, 5H, Ph)
H	*o*-$CH_3C_6H_4NO$	904	811	2.53(s, 3H, CH_3), 5.86(s, 5H, C_5H_5), 5.96(s, 5H, C_5H_5), 7.20(m, 4H, benzenoid protons)
CH_3	PhNO	896	809	1.90(s, 6H, CH_3), 5.43, 5.73, 6.00(m, 8H, cyclopentadienyl ring protons), 7.05–7.90(m, 5H, benzenoid protons)
CH_3	*o*-$CH_3C_6H_4NO$	895	812	1.98(s, 6H, CH_3), 2.53(s, 3H, CH_3), 5.43, 5.80, 6.03(m, 8H, cyclopentadienyl ring protons), 7.25(m, 4H, benzenoid protons)

[a] Satisfactory C, H, N analyses were obtained for *3*. [b] KBr disc. [c] $CDCl_3$ with tetramethylsilane as internal standard.

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