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Preliminary communication

INTERACTION OF ARYL AZIDES WITH TUNGSTEN COMPLEXES. THREE NEW TYPES OF REACTIONS YIELDING COORDINATED RN_3PR_3, RN_3H, AND RN.

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Summary

The first phosphazide and monosubstituted triazenide complexes have been prepared by allowing either phenyl or p-tolylazide to react with $WBr_2(CO)_3(PPh_3)_2$ and $WH(CO)_2(NO)(PPh_3)_2$ under mild conditions to yield $WBr_2(CO)_3(RN_3PPh_3)$ and $W(RN_3H)(CO)(NO)(PPh_3)_2$, respectively. The same aryl azides react with $W(CO)_2(S_2CNEt_2)_2(PPh_3)$ to yield dinitrogen and the aryl nitrene complex, $W(CO)(RN)(S_2CNEt_2)_2$. The coordinated RN_3PR_3 and RN_3H are of special interest because they may aid in understanding the mechanism of nitrene and amide formation from azides.

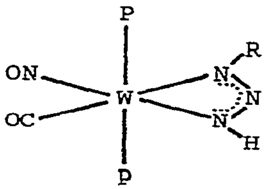
In order to develop viable syntheses of nitrene complexes, we have undertaken a study of reactions of organic azides with a number of transition metal complexes, especially those containing tungsten. We now report the preparations of complexes containing a coordinated tetraarylphosphazide ligand[1], a monoaryl triazenido ligand, and an aryl nitrene ligand. There are literature reports of organic azides acting on transition metal complexes to give substituted isocyanate[2], diazene[3], tetraazadiene[4], amide[5], and ureylene[5] ligands, but to our knowledge, stable complexes containing RN_3PR_3 and RN_3H were heretofore unknown. The only prior report of stable nitrene complexes formed from organic azides involved the use of fluoralkyl azides [7]. All reported reactions proceeded in dry methylene chloride nearly quantitatively (determined spectroscopically) with isolated yields ranging from 50 to 85 percent. Careful gas evolution studies yielded the identity and quantity of gaseous products. All C,H and N elemental analyses performed on each of the newly reported compounds were quite satisfactory.

Para-tolyl azide reacts (20°, 15 min) with $WBr_2(CO)_3(PPh_3)_2$[8] to form orange crystals of I. The azide seems to first act by

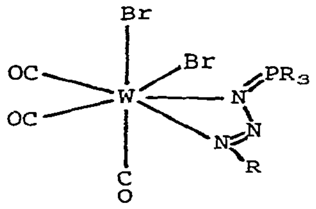
$$WBr_2(CO)_3(PPh_3)_2 + 2RN_3 \longrightarrow WBr_2(CO)_3(RN_3PPh_3) + RNPPh_3 + N_2$$

I

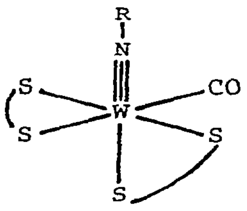
removing one of the coordinated phosphines followed by insertion. In view of the ease at which the starting material looses CO to form $WBr_2(CO)_2(PPh_3)_2$, the absence of CO loss is surprising. However, longer reaction times of several hours produce a brown, carbonyl-containing product with concomitant CO evolution. I is stable in the solid state and in solution for extended periods at low temperature. It reacts with excess triphenylphosphine and sodium diethyldithiocarbamate to remove the phosphazide ligand. The IR spectrum shows ν(CO) at 2037, 1948, 1892 cm^{-1} and no distinguishable bands due to the N_3 group above 1500 cm^{-1}; ^1H NMR spectrum has signals at 2.4 δ (singlet, 3H), 7.2 δ (AA'BB' quartet, 4H), 7.8 δ (multiplet, 15H). The ^{31}P NMR spectrum



II



I



III

shows one broadened singlet (14Hz FWHM) at +42.0 δ (external H_3PO_4 reference). The absence of P-W coupling and the breadth of the resonance indicates that the phosphorus is attached to nitrogen and not tungsten.

In the presence of the W(0) hydride, $WH(CO)_2(NO)(PPh_3)_2$[9], p-tolyl azide appears to undergo an alpha-insertion reaction

$$WH(CO)_2(NO)(PPh_3)_2 \xrightarrow{RNCNR} W(RNCHNR)(CO)(NO)(PPh_3)_2 + CO$$

$$WH(CO)_2(NO)(PPh_3)_2 \xrightarrow{RN_3} \underset{\text{II}}{W(RN_3H)(CO)(NO)(PPh_3)_2} + CO$$

(20°, 10 min) to form deep red crystals of II. Since one equivalent of CO is evolved in the reaction, the monotolyltriazenido ligand is probably chelating. The somewhat broadened ^1H NMR resonance of the unique triazene proton is clearly visible, and the strong spectroscopic similarity of II with the 1,3-ditolyltriazenido analogue, $W(RN_3R)(CO)(NO)(PPh_3)_2$[9], suggests that the unique proton lies on the terminal nitrogen atom. The insertion reactions seem to be general. Under the same conditions with the tungsten hydride, ditolylcarbodiimide undergoes beta-insertion with CO loss to form the analogous 1,3-ditolylformamidinato ligand; with $ReH(CO)_2(PPh_3)_3$, an excess of tolyl azide also yields $Re(RN_3H)(CO)_2(PPh_3)_2$ and the respective phosphinimine. The IR spectrum of II shows ν(CO) at 1870 cm^{-1} and ν(NO) at 1610 cm^{-1}; ^1H NMR spectrum has signals at 2.3 δ (singlet, 3H), 6.6 δ (AA'BB' quartet, 4H), 7.3 δ (multiplet, 30H), 8.0 δ (singlet, 1H).

When p-tolyl azide reacts (37°, 30 min) with $W(CO)_2(Et_2dtc)_2(PPh_3)$[10] green crystals of the tolyl nitrene complex III are produced.

$$W(CO)_2(Et_2dtc)_2(PPh_3) + 2RN_3 \longrightarrow \underset{\text{III}}{W(CO)(RN)(Et_2dtc)_2} + CO + 2N_2 + RNPPh_3$$

Although formally similar to the first reaction, this third reaction takes a different course yielding an arylnitrene complex. At 20° the reaction requires several hours to complete, and an unisolable yellow intermediate is visually detectable. It is noteworthy that phenyldiazomethane undergoes a similar reaction with $W(CO)_2(Et_2dtc)_2(PPh_3)$ under the same conditions as phenyl or tolyl azide to yield brown crystals of $W(CO)(PhCH)(Et_2dtc)_2$, the phenylcarbene analogue of III. Unlike III which can be an 18-electron complex if the nitrene is a linear, 4-electron donor ligand, the carbene complex is a 16-electron complex like $Mo(CO)_2(Et_2dtc)_2$[11].

The IR spectrum of III shows ν(CO) at 1912 cm^{-1} and ν(CN) at 1500 cm ^{1}; ^{1}H NMR spectrum has signals at 1.3 δ (triplet, 6H), 1.4 δ (triplet, 6H), 3.7 δ (multiplet, 8H), 2.2 δ (singlet, 3H), 7.0 δ (singlet, 4H).

Earlier workers using aryl azides failed to produce nitrene complexes probably because they worked mostly with d^8 and d^{10} complexes. Only perfluoroalkyl azides gave stable products. Our work with d^4 complexes (W(II) and Re(III)) shows that aryl azides are indeed good sources of nitrene ligands, and we are expanding our work to include d^2 and d^6 complexes. The metal-containing reaction products of organic azides with metal complexes rarely retain all three nitrogen atoms of the original azide; ligands such as nitrenes and amides are often formed. For this reason, we are presently studying the reactions of I and II at temperatures above 20° in order to better understand the mechanism of N_2 loss.

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References

1. Regarding nomenclature, see H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 4 (1921) 861.
2. J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun and J. W. Kang, *J. Amer. Chem. Soc.*, 90, (1968) 5430; S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organometal. Chem.*, 88 (1975) 237.
3. M. Dekker and G. R. Knox, *Chem. Commun.* (1967) 1243.
4. S. Otsuka and A. Nakamura, *Inorg. Chem.*, 7 (1968) 2542; R. J. Doedens, *Chem. Commun.*, (1968) 1271.
5. W. Beck and M. Bauder, *Chem. Ber.*, 103 (1970) 583.
6. W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, *J. Chem. Soc.*, Dalton (1974) 298; R. J. Doedens, *Inorg. Chem.*, 7, (1968) 2323.
7. M. J. McGlinchey and F.G.A. Stone, *Chem. Commun.*, (1970) 1265.
8. M. W. Anker, R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 20 (1967) 9.
9. B. L. Haymore, unpublished results.
10. G. J. Chen, R. O. Yelton and J. W. McDonald, *Inorg. Chim. Acta*, 22 (1977) 249.
11. R. Colton, G. R. Scollary and I. B. Tomkins, *Aust. J. Chem.*, 21 (1968) 15.