

ortho-METALATION REACTIONS
III*. COMPLEXES FROM REACTIONS BETWEEN DODECACARBONYL-
TRIRUTHENIUM AND AZOBENZENE OR *o*-SEMIDINE

M. I. BRUCE, M. Z. IQBAL AND F. G. A. STONE

Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

(Received March 18th, 1971)

SUMMARY

The major products from the reaction between dodecacarbonyltriruthenium and azobenzene (Hazb) are a trinuclear complex $(C_{12}H_{10}N_2)Ru_3(CO)_9$, containing a rearranged ligand related to *o*-semidine (semH₂), and the complexes are semRu₂(CO)₆, and [azbRu(CO)₃]₂. Similar reactions with *o*-semidine gave the dinuclear ruthenium complexes sem₃Ru₂(CO)₄ and sem₂Ru₂(CO)₄, and the trinuclear compound sem₂Ru₃(CO)₈.

INTRODUCTION

Reactions of various iron carbonyls with azobenzene and substituted azobenzenes give products which depend on the substituent in the benzene ring. Thus, azobenzene gives² only one iron complex, in low yield (3.5%), shown by chemical, spectroscopic, and X-ray methods³ to be the *o*-semidine** (H₂sem) derivative (I). As found previously with complexes of cobalt⁴, rhodium⁵ and molybdenum⁶, the azobenzene nucleus evidently rearranges to the *o*-phenylenediamine skeleton. From *p*-azoanisole, the analogous complex (II) is obtained in 22% yield, and is accompanied by a small amount of the substituted bis-2*C,N'*-(phenylazo)phenyl complex (III). *p*-Azotoluene gives the corresponding binuclear complex (IV), together with a trinuclear compound formulated as (V), both obtained in only very small amounts.

RESULTS AND DISCUSSION

Herein we describe the reaction between azobenzene and dodecacarbonyltriruthenium. The well-known⁷ stability of the metal-metal bonds in Ru₃(CO)₁₂ suggested that higher yields of polynuclear complexes might be obtained, which would enable their physical properties to be studied in more detail. This hope was justified, and this paper describes the complexes obtained.

In refluxing petroleum ether at ca. 100°, reaction between Ru₃(CO)₁₂ and

* For Part II see ref. 1.

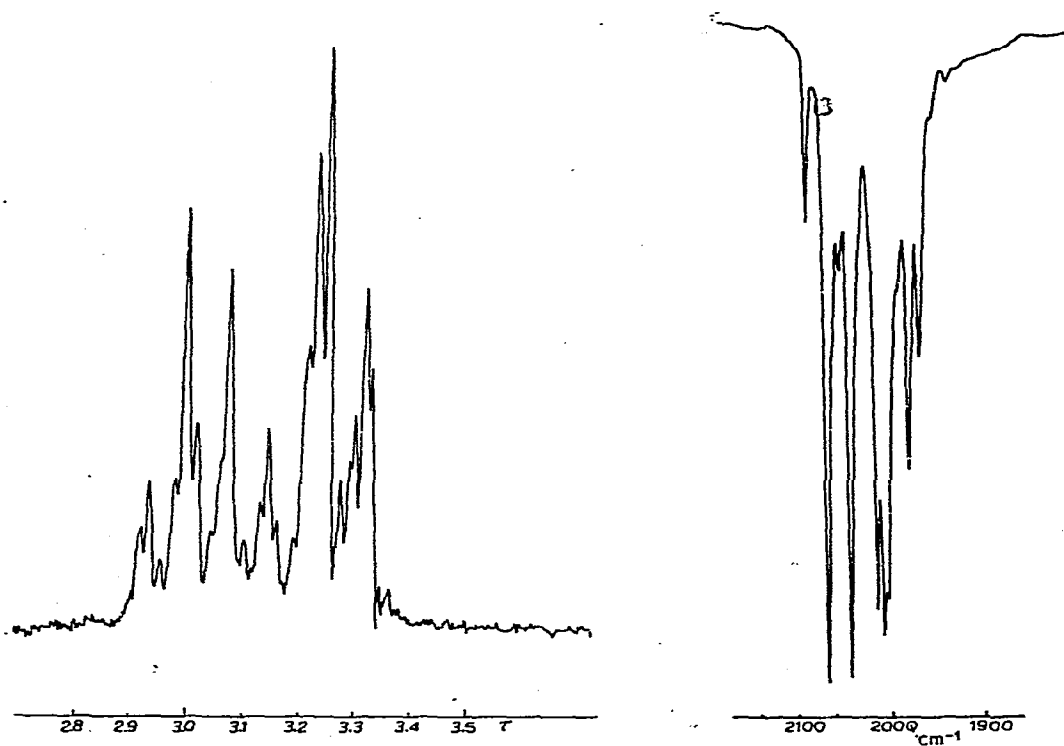
** *o*-Semidine = *N*-phenyl-*o*-phenylenediamine; sem = -NHC₆H₄NPh-. azb = 2*C,N'*-(phenylazo)phenyl.

TABLE 1

MELTING POINTS AND ANALYTICAL DATA

No.	Complex	M.p. ^a (°C)	Analyses, found (calcd.) (%)				Mol. wt., found (calcd.)
			C	H	N	O	
(VI)	semRu ₃ (CO) ₉	190	34.1 (34.1)	1.5 (1.3)	3.6 (3.8)		740 ^b (740)
(VII)	semRu ₂ (CO) ₆	128–130	39.1 (40.4)	1.8 (2.8)	5.1 (5.8)		
(VIII)	azb ₂ Ru ₂ (CO) ₆	115	49.3 (49.2)	3.0 (2.5)	7.8 (7.6)	13.1 (13.1)	761 ^c (732)
(IX)	(H ₂ sem) ₃ Ru ₂ (CO) ₄	131	55.35 (55.7)	3.5 (3.5)	9.5 (9.7)	7.5 (7.4)	810 ^c (860)
(X)	(C ₁₂ H ₁₂ N ₂ O) ₃ Ru ₂ (CO) ₄	300	52.2 (52.85)	3.7 (3.3)	9.2 (9.2)	12.5 (12.2)	2287 ^d (908)
(XI)	(H ₂ sem) ₂ Ru ₃ (CO) ₈	184	43.9 (43.1)	2.0 (2.2)	6.0 (6.3)	14.2 (14.3)	
(XII)	(H ₂ sem) ₂ Ru ₂ (CO) ₄	132	48.4 (49.5)	3.0 (3.0)	8.2 (8.2)		

^a With decomposition. ^b Mass spectrometry. ^c Osmometrically, in chloroform. ^d Found Ru 22.9, Calcd. 22.1%.

Fig. 1. Proton NMR spectrum of semRu₃(CO)₉.Fig. 2. The carbonyl region of the IR spectrum of semRu₃(CO)₉.

azobenzene affords three complexes, which can be conveniently separated by chromatography on Florisil. The most tractable compound, obtained in yields approaching 20%, is eluted first, and forms deep red crystals (VI). Analytical data (Table 1) suggest the formula $C_{12}N_{10}N_2Ru_3(CO)_9$, indicating that it is an analogue, namely $semRu_3(CO)_9$, of the iron complex (V). Degradation with lithium aluminum hydride gave *o*-semidine, lending some support to this interpretation.

The proton NMR spectrum (Fig. 1) contains a complex set of resonances between $\tau 2.92 - 3.36$, the region in which *o*-semidine resonances appear. The spectra of the cyclopentadienyl-molybdenum complexes containing *o*-semidine ligands, described earlier⁶, also contain a complex resonance between $\tau 2.4 - 3.5$, which is similar in overall appearance to that observed in the spectrum of complex (VI). No NH resonance is observed, even in quite concentrated solutions, and in contrast with the other *o*-semidine complexes discussed, no $\nu(NH)$ band is found in the infrared spectrum. No resonance is found in the region $\tau 10 - 40$, showing that no metal-bonded protons are present. The carbonyl region of the infrared spectrum is complex (Fig. 2).

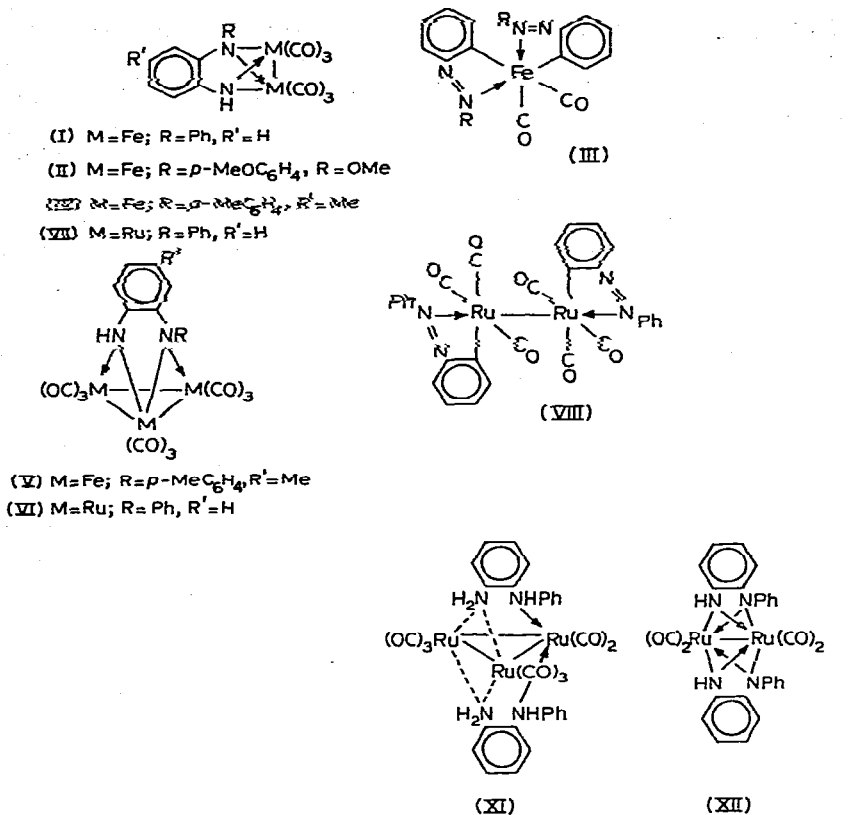
The highest ion in the mass spectrum (centred on m/e 740) correspond to the parent ions $[C_{12}H_{10}N_2O_9Ru_3]^+$; major ruthenium-containing ions are formed by loss of CO groups, and breakup of the ligand commences while attached to the Ru_3 cluster. Strong doubly-charged ions $[M - nCO]^{2+}$ ($n=4-9$), and at m/e 432 ($[M - 9CO - 2N]^{2+}$), are also found. Metal-free ions have only low intensity, and include $[C_{12}H_{10}N_2]^+$ and $[C_6H_5NH_2]^+$. The much higher yield of the ruthenium complex (20%), compared to the iron derivative (0.16-0.3%) reflects the relative strengths of the metal-metal bonds in the parent carbonyls.

The final assignment of the structure of this interesting complex must await the results of a single-crystal X-ray investigation.

A second complex, obtained in only ~8% yield, is an unstable, rust coloured solid, and analytical data give the formula as $C_{12}H_{10}N_2Ru_2(CO)_6$ (VIII). The infrared spectrum in the carbonyl stretching region shows a band pattern consistent with the presence of an $Ru_2(CO)_6$ group, and degradation in the usual way gave *o*-semidine. The instability of this complex in solution precluded the recording of the proton NMR spectrum, only a rather broad signal between $\tau 2.5 - 3.3$ being found, with no fine structure resolved. The general similarity in properties with the iron complex (I) suggests that complex (VII) should be formulated as $semRu_2(CO)_6$, containing two $Ru(CO)_3$ groups linked by a metal-metal bond, and bridged by an *o*-semidine moiety as shown.

The other major product, isolated from this reaction in 40% yield is a dark brown solid, shown to have the formula $(C_{12}H_9N_2)_2Ru_2(CO)_6$ (VIII). Degradation with lithium aluminium hydride gave azobenzene, and the proton NMR spectrum confirmed the presence of chelated, *ortho*-metalated (phenylazo)phenyl ligands, showing resonances between $\tau 1.7 - 3.2$. Bromination gave the bromine-bridged dimeric $[azbRu(CO)_2Br]_2^+$ suggesting that the azo ligands chelate each metal atom, rather than bridge the two ruthenium atoms. The only structure consistent with the properties of this complex is one containing two $azbRu(CO)_3$ groups linked by a metal-metal bond, although it has not been possible to determine the absolute configuration.

The reaction between azobenzene and $Ru_3(CO)_{12}$ is thus more versatile and gives a wider range of products in higher yields, than the corresponding reaction with iron carbonyls. All the complexes so far found retain at least one metal-metal bond,



and no compounds of the type $\text{azb}_2\text{Ru}(\text{CO})_2$ were formed. As with the iron carbonyl reactions, the mechanism of the rearrangement of azobenzene to *o*-semidine remains obscure.

The reaction between *o*-semidine and $\text{Ru}_3(\text{CO})_{12}$ was also examined to determine whether either of the complexes (VI) or (VII) could be isolated from this reaction. However, neither complex was found in the reaction mixture. Instead, a brick-red complex (IX) precipitated, and was purified by washing with benzene and light petroleum. Attempted recrystallisation of this material from dichloromethane, chloroform, or acetone, the only solvents in which it appeared to dissolve, resulted in rapid decomposition to a purple material. Complex (IX) analysed for $(\text{H}_2\text{sem})_3\text{Ru}_2(\text{CO})_4$; in chloroform, it is apparently a monomer, and the mass spectrum shows ions corresponding to *o*-semidine, and degradation with lithium aluminium hydride gave *o*-semidine.

The proton NMR spectrum gave a complex resonance between $\tau 2.55\text{--}3.60$, with no obvious resemblances to the fine structure found with either azobenzene or *o*-semidine complexes. However, rapid decomposition occurred, and the multiplet quickly broadened. The insolubility of this complex suggests that it may be polymeric. The carbonyl region of the IR spectrum of the solid is complex.

The purple solution obtained from complex (IX) in polar solvents afforded a deep purple solid (X) on evaporation, which still showed two broad $\nu(\text{CO})$ bands in

the infrared spectrum. A complete analysis gave an empirical formula $C_{40}H_{36}N_6O_7Ru_2$, or $(H_2sem)_3Ru_2(CO)_4O_4$, suggesting that oxidation of (IX) has occurred. Molecular weight determinations gave a value of 2287 ($CHCl_3$), corresponding to the presence of six or seven ruthenium atoms in the solute molecules, *i.e.* a low polymer. The proton NMR spectrum consisted of a broad signal between $\tau 2.2-4.2$, which was uninformative. The intense colouration associated with this material is reminiscent of the products obtained by oxidation of diamines, in agreement with the analytical values.

Chromatography of the solution obtained from the reaction between $Ru_3(CO)_{12}$ and *o*-semidine gave two more complexes. The first, a rust-red solid (XI), analysed for $(H_2sem)_2Ru_3(CO)_8$ and gave a well-defined IR spectrum in the carbonyl stretching region. Unfortunately a mass spectrum could not be obtained, and decomposition in solution prevented osmometric molecular weight measurement. A plausible structure is illustrated, and is based on an assumption that the Ru_3 cluster is preserved, with the semidine ligands acting as four-electron donors. In contrast to (VI), three bands in the N-H region of the IR were observed. The second complex (XII) [$\nu_{max}(NH)$ 3278 cm^{-1}] was even more unstable; analysis suggested the formula $C_{28}H_{20}N_4O_4Ru_2 [(H_2sem)_2Ru_2(CO)_4]$, and the mass spectrum showed ions consistent with the presence of an *o*-semidine moiety.

Both series of reactions described above suggest that the chemistry of ruthenium carbonyl species with nitrogen-containing ligands is complex and deserving of further study.

EXPERIMENTAL

Spectroscopic studies were carried out using the instruments described elsewhere¹. Infrared spectra are collected in Table 2. Solvents were dried and distilled before use. Chromatography was carried out on columns of Florisil, initially packed in light petroleum. All reactions were carried out under a nitrogen atmosphere.

Reactions of azobenzene with $Ru_3(CO)_{12}$

Dodecacarbonyltriruthenium (1.2 g, 1.9 mmoles) and azobenzene (1.6 g, 8.8 mmoles) in petroleum ether (75 ml) were refluxed for 3.5 h. After removal of solvent, chromatography gave several fractions.

- (i) Light petroleum eluted a mixture of azobenzene and complex (VI). The former was removed by sublimation ($100^\circ/0.1$ mm), and recrystallisation of the residue (light petroleum) gave deep red needles of (VI) (284 mg, 20%), subliming slowly at 150° (0.1 mm).
- (ii). A deep red oil, not further investigated, was eluted with a 1/1 light petroleum/benzene mixture.
- (iii). Benzene eluted complex (VII), which was recrystallised (light petroleum/ether) to give a rust-coloured solid (90 mg, 8.6%), slightly unstable in solution.
- (iv). Complex (VIII) was eluted with a 1/1 benzene/ether mixture, and could be recrystallised (light petroleum/ether) to give a light brown solid (390 mg, 42%).

Under slightly different conditions, the yields of complexes (VI), (VII), and (VIII) were respectively 20, 3, and 46%, and they were accompanied by a fourth complex, eluted with benzene/ether (1/1) and crystallised from ether/light petroleum to give a dark brown solid, showing $\nu(CO)$ at 2037 and 1973 cm^{-1} (838 mg), m.p.

TABLE 2
INFRARED SPECTRA OF THE COMPLEXES

No.	Complex	$\nu(\text{CO})(\text{cm}^{-1})$	Other bands (cm^{-1})
(VI)	$\text{semRu}_3(\text{CO})_9$	2092 w, 2071 vs, 2048 vs, 2020 s, 2013 vs, 2010 vs, 1986 ms, 1976 m ^a	3074 w, 1584 ms, 1446 ms, 1302 m, 1276 w, 1243 m, 1220 s, 1172 w, 1153 w, 1078 ms, 1031 ms, 1001 w, 980 w, 965 w, 907 w, 874 w, 834 w, 784 s, 730 vw, 705 s, 642 s ^b
(VII)	$\text{semRu}_2(\text{CO})_6$	2054 ms, 2021 m, 1973 vs, br ^c	3302 m, br, 3046 w, 1656 w, 1648 w, 1595 ms, 1544 m, 1489 w, 1448 m, 1315 m, br, 1259 sh, 1232 ms, 1167 w, 1157 w, 1111 m, 1076 m, 1043 w, 1029 m, 1003 w, 916 vw, 899 w, 872 vw, 837 w, 807 w, 775 s, 761 s, 732 s, 701 s ^b
(VIII)	$[\text{azbRu}(\text{CO})_3]_2$	2098 m, 2035 vs, 1975 s, 1953 ms ^c	3043 w, 1583 s, 1550 w, 1428 s, 1362 m, 1271 w, 1229 s, 1170 w, 1157 m, 1111 m, 1078 m, 1030 m, 1005 vw, 961 vw, 912 w, 886 w, 841 w, 808 w, 776 s, 760 ms, 733 s, 701 s ^b
(IX)	$(\text{H}_2\text{sem})_3\text{Ru}_2(\text{CO})_4$	2038 ms, 2021 vs, 1966 s, 1951 sh ^c 2030 s, 2007 vs, 1987 sh, 1965 w, 1945 s, 1929 s, 1910 sh, 1898 sh ^b	3372 m, br, 3329 m, 3301 w, 3278 ms, 3205 ms, 3047 m, 1592 s, 1580 sh, 1542 vw, 1452 s, br, 1414 m, 1325 sh, 1310 s, 1289 ms, 1242 s, 1222 s, 1198 ms, 1183 ms, 1166 sh, 1158 m, 1111 ms, 1103 sh, 1083 m, 1069 m, 1043 ms, 1031 sh, 1001 m, 972 vw, 942 w, 922 w, 910 w, 893 m, 888 sh, 863 ms, 834 m, 822 sh, 812 ms, 762 s, 745 sh, 740 s, 710 s, 701 s, 662 m, 643 ms ^b
(X)	$(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})_3\text{Ru}_2(\text{CO})_4$	2035 vs, 1975 vs ^c	1591 s, 1193 ms, 1153 s, 1075 ms, 1029 ms, 1003 ms, 923 ms, 835 ms, br, 752 s, 731 sh, 703 s ^b
(XI)	$(\text{H}_2\text{sem})_2\text{Ru}_3(\text{CO})_8$	2071 s, 2045 vw, 2023 w, 2006 vs, 1979 s, 1958 vw, 1951 vw, 1929 s ^a 2059 vs, 2010, 1998 vs, 1988 sh, 1972 vs, br, 1956 sh, 1923 s, 1909 s, b	3058 m, 2952 w, 1591 s, 1483 s, 1442 s, 1397 ms, br, 1185 ms, 1153 s, 1057 ms, 1029 ms, 923 m, 815 s, 753 s, 703 s ^d
(XII)	$(\text{H}_2\text{sem})_2\text{Ru}_2(\text{CO})_4$	2041 sh, 2027 sh, 2016 vs, 1968 s, br, 1944 sh ^c 2010 s, 1958 s, br, b	3348 m, 3235 m, 3202 ms, 1598 sh, 1591 s, 1491 s, 1281 ms, 1236 s, 1209 s, 1194 s, 1178 w, 1158 m, 1107 m, 1083 w, 1033 w, 1005 vw, 986 ms, 971 ms, 947 m, 903 vw, 887 vw, 863 w, 833 w, 803 ms, 765 s, 755 s, 751 sh, 743 sh, 733 s, 702 ms ^b

^a Cyclohexane. ^b Nujol. ^c Chloroform. ^d Hexachlorobutadiene.

179° dec. The complex was unstable, and not further characterised (Found: C, 47.7; H, 3.0; N, 7.4; O, 12.0%; mol. wt., 543.)

Degradation reactions

The complex (~100 mg) in ether was treated with a filtered ethereal solution of lithium aluminium hydride (~100 mg), and the mixture stirred at 0° for 10 min. Excess hydride was destroyed by careful dropwise addition of ethanol, and the solvents were removed. Extraction with ether, followed by chromatography on Florisil, gave orange azobenzene, eluted with light petroleum, or white *o*-semidine, eluted with ether, as appropriate, each being identified by comparison with an authentic sample. Recovery of the ligand was usually 30–75%.

Reaction of complex (VIII) with bromine. A solution of complex (VIII) (10 mg, 0.014 mmole) in CCl₄ (5 ml) was treated dropwise with 5% bromine/CCl₄ (1 ml) at room temperature, and the mixture was stirred for 30 min. Filtration, evaporation and recrystallisation from light petroleum gave dicarbonyl[2*C,N'*-(phenylazo) phenyl]bromoruthenium (2 mg, 17%), m.p. 217–220°, shown to be identical with an authentic sample¹.

Reactions of *o*-semidine with Ru₃(CO)₁₂

A filtered solution of dodecacarbonyltriruthenium (1.2 g, 1.9 mmoles) and *o*-semidine (1.6 g, 8.8 mmoles) in petroleum ether (75 ml) was refluxed for 3.5 h. A brick-red solid separated, which was filtered, and washed with benzene and light petroleum to give complex (IX) (543 mg, 49%). Evaporation of the filtrate and chromatography gave, with benzene, a red fraction which afforded brick red crystals of complex (XI) (58 mg, 3.5%) from light petroleum. Benzene/ether (1/1) eluted the unstable complex (XII) as a rust-coloured solid, which was recrystallised from a light petroleum/ether mixture (68 mg, 8%). Acetone eluted a deep violet compound (X) (865 mg, 39%), obtained pure by recrystallisation from dichloromethane/*n*-hexane mixtures.

Complex (X) could also be obtained by treating complex (IX) with dichloromethane, chloroform, or acetone.

ACKNOWLEDGEMENTS

M.Z.I. thanks the Panjab University, Lahore, West Pakistan, for study leave during which this work was carried out. We also thank Professor P. L. Pauson for further information concerning complex (V).

REFERENCES

- 1 M. I. BRUCE, M. Z. IQBAL AND F. G. A. STONE, *J. Chem. Soc. A*, in press.
- 2 M. M. BAGGA, W. T. FLANNIGAN, G. R. KNOX AND P. L. PAUSON, *J. Chem. Soc. C*, (1969) 1534.
- 3 P. E. BAIKIE AND O. S. MILLS, *Inorg. Chim. Acta*, 1 (1967) 55.
- 4 T. JOH, N. HAGIHARA AND S. MURAHASHI, *Bull. Chem. Soc. Jap.*, 40 (1967) 661.
- 5 T. JOH, N. HAGIHARA AND S. MURAHASHI, *Nippon Kagaku Zasshi.*, 88 (1967) 786.
- 6 M. I. BRUCE, M. Z. IQBAL AND F. G. A. STONE, *J. Chem. Soc. A*, (1970) 3204.
- 7 M. I. BRUCE AND F. G. A. STONE, *Angew. Chem.*, 80 (1968) 460; *Angew. Chem., Int. Ed. Engl.*, 7 (1968) 427.