## Synthesis and Reactions of a New Neutral Diazo Complex of Iridium(I)

Sir:

It is now well established that the aryldiazo ligand, N_2R^+, shows varying modes (A, B, C, Figure 1) of attachment to transition metal systems, and that such variations may be used as a sensitive probe of the metal center and its reaction chemistry.[1-7] In this sense the N_2R^+ ligand shows amphoteric character as do NO^+ [8] and SO_2.[9] Although the literature[10] is repleat with a wide variety of diazo *molecules,* N_2R, essentially no reaction chemistry of such molecules with transition metals has evolved. Recently[11] the coordination of diazofluorene, R = fluorene, was established as side-on (D), there being no counterpart known among N_2R^+ complexes at this time. A diazomethane complex of manganese shows a unique structure in which the neutral ligand bridges three metal atoms.[12] Moreover, we have established the totally linear geometry (E) for $R = B_{10}H_8SMe_2$,[13] and again there is no counterpart in N_2R^+ structures. On the basis of the three known examples, neutral N_2R ligands may be much more versatile than N_2R^+ ligands in their modes of bonding to metal complexes. However, the comparative structural and reaction chemistry of N_2R^+ and N_2R complexes of transition metals is hampered by the essentially complete absence of transition metal–N_2R complexes.

Here we wish to report a facile synthetic route to a variety of new iridium–N_2R species, in which N_2R = 2, 3, 4, 5-tetrachlorodiazocyclopentadiene, $N_2C_5Cl_4$, and to contrast the reaction chemistry of the key compound $IrCl(N_2C_5Cl_4)$-$(PPh_3)_2$ (I) with related systems $IrClX(PPh_3)_2$ where X = CO,[14] NO^+,[15] and N_2Ph^+.[16] Compound I is prepared in one step from $IrCl(CO)(PPh_3)_2$ according to

$$IrCl(CO)(PPh_3)_2$$

$$\xrightarrow[\substack{N_2C_5Cl_4,\ 0\ °C}]{\text{CHCl}_3/\text{EtOH, ArCON}_3} IrCl(N_2C_5Cl_4)(PPh_3)_2 \quad (1)$$
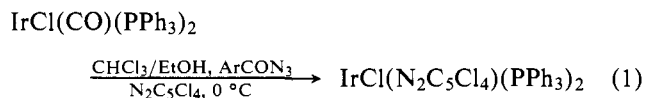
It has been characterized by the usual analytical and spectroscopic methods and by a complete crystal structure analysis (R = 0.047). Figure 2 shows the inner coordination sphere of the complex. Note that the mode of attachment (A) is the fourth one to be exhibited among the four known structures of transition metal–N_2R complexes.

Compound I reacts with phosphines, phosphites, isocyanides, nitrosyl, and diazonium ions to form the respective five-coordinate species (Table I). Upon formation of the five-coordinate complex, $IrCl(N_2C_5Cl_4)L(PPh_3)_2$, $\nu(NN)$ sharply decreases by ~400 cm^{-1} when L = t-BuNC and by 200 cm^{-1} when L = tertiary phosphine. The value of $\nu(NN)$ also decreases upon coordination of $NO\cdot$ and PhN_2^+; isotopic labeling experiments using $^{15}NO^+$ and $^{15}NNPh^+$ are in progress.

Carbon monoxide and SO_2 displace the diazo ligand of compound I to give $IrCl(CO)(PPh_3)_2$ and $IrCl(SO_2)(PPh_3)_2$.[17] The diazo ligand does not react with $IrCl(CO)(PPh_3)_2$ nor with the thiocarbonyl analogue $IrCl(CS)(PPh_3)_2$.[18]

The reaction chemistry of compound I depends upon the

Figure 1. Pictorial representation of bonding modes of transition metal diazo complexes. Multiple bonds are not shown.

Figure 2. The inner coordination sphere with some bond distances for $IrCl(N_2C_5Cl_4)[P(C_6H_5)_3]_2$.

electronic and steric characteristics of the incoming ligand. Thus cationic ligands such as NO^+ and PhN_2^+ react with compound I to give five-coordinate products. These complexes are particularly interesting in that they contain two amphoteric ligands. The observed $\nu(NO)$ and $\nu(NN)$ stretching frequencies of the $IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2^+$ complex are low (1522, 1497, and 1450 cm^{-1}), consistent with a bonding mode of the N_2R ligand significantly different from that in compound I. The values of $\nu(NN)$ for the complexes $IrCl(N_2C_5Cl_4)(L)(PPh_3)_2$, L = $PMePh_2$ and PhN_2^+, suggest that the bonding mode of the N_2R ligand may be identical in these two complexes.

The reaction chemistry of compound I resembles, to a point, the chemistry of the cationic aryldiazo complex $IrCl(N_2Ph)$-$(PPh_3)_2^+$.[16] Both complexes form five-coordinate adducts with phosphines and isocyanides and exhibit similar decreases in the values of $\nu(NN)$ upon coordination of these ligands. However, the reactions of compound I with CO, NO^+, and N_2Ph^+ are very different. The neutrality of complex I as opposed to $IrCl(N_2Ph)(PPh_3)_2^+$ is certainly one obvious feature.

Structurally, the coordinated $N_2C_5Cl_4$ and PhN_2^+ [19] complexes are similar; both contain singly-bent diazo linkages (Ir–N(1)–N(2) = 174.9, 176.1°), with the diazo R group perpendicular to the P–P vector. The N(1)–N(2)–C(1) angles (141, 126°) and the N(2)–C(1) (1.35, 1.45 Å) distances are markedly different in the two complexes; the N–N–C angle of the N_2R complex is closer to 180°, but this may only be a function of the increased steric bulk of the chlorine atoms on the cyclopentadiene ring. The N(2)–C(1) distance of the N_2R complex is identical with that observed for uncoordinated neutral diazo ligands;[20] however, the molecular structure of

Table I

Compd[a]	Appearance	Infrared data[b]
$IrCl(N_2C_5Cl_4)(PPh_3)_2$	Dark green	$\nu(NN)$ = 1858; $\nu(IrCl)$ = 348
$IrCl(N_2C_5Cl_4)(N_2Ph)(PPh_3)_2^+$	Orange-brown	$\nu(NN)$ = 1678, 1665
$IrCl(N_2C_5Cl_4)(PMePh_2)(PPh_3)_2$	Red-brown	$\nu(NN)$ = 1660
$IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2^+$	Orange-yellow	$\nu(NO, NN)$ = 1522, 1497, 1450; $\nu(IrCl)$ = 330
$IrCl(N_2C_5Cl_4)(t\text{-BuNC})(PPh_3)_2$	Dark purple	$\nu(NN)$ = 1455; $\nu(CN)$ = 2210
$N_2C_5Cl_4$	Dark yellow	$\nu(NN)$ = 2105

[a] A representative group of the compounds prepared; frequencies given as cm^{-1}; C, H, and N analyses are satisfactory for all compounds; spectra taken in perfluorokerosene and Nujol mulls; anions are always PF_6^-. [b] $\nu(NN)$ and $\nu(NO)$ for the metal complexes are tentatively assigned awaiting ^{15}N labeling studies.
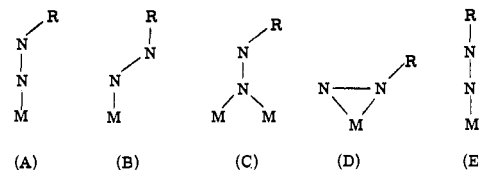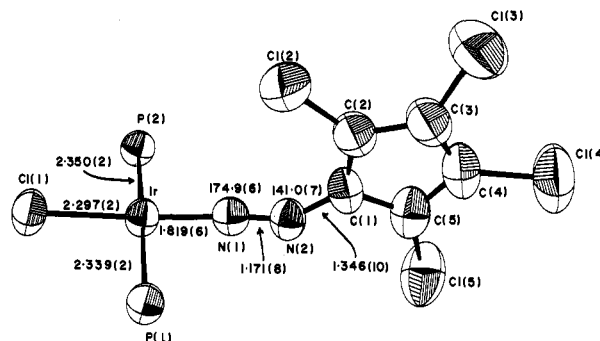
the $N_2C_5Cl_4$ molecule is not known. The Ir–N(1) (1.819, 1.794 Å) and N(1)–N(2) (1.171, 1.159 Å) distances, while similar, are consistent with less π back-bonding from metal to atom N(1) in the N_2R species.

We believe that the route to a variety of metal–N_2R complexes described here is a general one and that the comparative reaction and structural chemistry of these complexes and their CO, NO$^+$, and N_2Ph^+ analogues will prove to be diverse and interesting.

References and Notes

(1) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 2713 (1973); K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 176 (1973).
(2) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B.*, **27**, 725 (1971).
(3) M. Cowie, B. L. Haymore, and J. A. Ibers, *Inorg. Chem.*, **14**, 2617 (1975); B. L. Haymore and J. A. Ibers, *ibid.*, **14**, 1369 (1975); B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 5369 (1975).
(4) A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Meyers, T. E. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973); B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, **14**, 541 (1975); S. Krogsrud and J. A. Ibers, *ibid.*, **14**, 2298 (1975).
(5) E. W. Abel, C. A. Burton, M. R. Churchill, and K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 268 (1974); M. R. Churchill and K. G. Lin, *Inorg. Chem.*, **14**, 1133 (1975).
(6) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969); S. Cenini, R. Ugo, and G. La Monica, *ibid.*, 3441 (1971); A. Garner and M. Mays, *J. Organomet. Chem.*, **67**, 153 (1974).
(7) W. E. Carroll and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1754 (1973); W. E. Carroll, M. E. Deane, and F. J. Lalor, *ibid.*, 1837 (1974); W. E. Carroll, F. A. Deeney, and F. J. Lalor, *ibid.*, 1430 (1974).
(8) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968); N. G. Connelly, *Inorg. Chim. Acta Rev.*, **6**, 47 (1972); R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975); D. Sutton, *J. Chem. Soc. Rev.*, **4**, 443 (1975).
(9) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966); K. W. Muir and J. A. Ibers, *ibid.*, **8**, 1921 (1969); D. C. Moody and R. R. Ryan, *J. Chem. Soc., Chem. Commun.*, 503 (1976); R. R. Ryan and P. G. Eller, *Inorg. Chem.*, **15**, 494 (1976); D. C. Moody and R. R. Ryan, *ibid.*, **15**, 1823 (1976); P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *ibid.*, **15**, 2768 (1976); R. R. Ryan, P. G. Eller, and G. J. Kubas, *ibid.*, **15**, 797 (1976).
(10) A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, **181**, 1000 (1958); D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem. Soc.*, **85**, 2529 (1963); H. E. Zimmerman and D. H. Paskovich, *ibid.*, **86**, 2149 (1964); N. Obata and I. Moritani, *Bull. Chem. Soc. Jpn.*, **39**, 1975 (1966); G. B. Ansell, *J. Chem. Soc. B*, **729** (1969); C. T. Presley and R. L. Sass, *Acta Crystallogr., Sect. B*, **26**, 1195 (1970); D. J. Abraham, T. G. Cochran, and R. D. Rosenstein, *J. Am. Chem. Soc.*, **93**, 6279 (1971); S. I. Murahashi, Y. Yoshimura, Y. Yamamoto, and I. Moritani, *Tetrahedron*, **28**, 1485 (1972); H. Hope and K. T. Black, *Acta Crystallogr., Sect. B*, **28**, 3632 (1972).
(11) A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2108 (1977).
(12) W. A. Herrmann, M. L. Ziegler and K. Weidenhammer, *Angew. Chem., Int. Ed. Engl.*, **15**, 368 (1976).
(13) K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, **16**, 3287 (1977).
(14) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968); J. P. Collman, *ibid.*, **1**, 136 (1968); R. Cobbledick, F. W. B. Einstein, N. Farrell, A. B. Gilchrist, and D. Sutton, *J. Chem. Soc., Dalton Trans.*, 373 (1977).
(15) C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969); 1459 (1969).
(16) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3052 (1973).
(17) A. C. Jesse, J. F. van Baar, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, **17**, L13 (1976).
(18) M. Kubota, *Inorg. Syn.*, in press.
(19) B. L. Haymore, private communication.
(20) T. H. Tulip and J. A. Ibers, *Acta Crystallogr.*, in press.

K. Dahl Schramm, James A. Ibers*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201
Received December 15, 1977

A Total Synthesis of Lasalocid A

Sir:

Lasalocid A (**1**), produced by *Streptomyces lasaliensis*, is a member of the class of naturally occurring ionophores known as polyether antibiotics.[1] Isolation,[2] structure elucidation,[3,4]
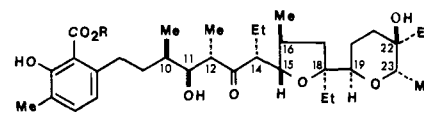
1, R = H (lasalocid A)
15, R = CH$_2$C$_6$H$_5$

biosynthesis,[5] and biological activity[6] of lasalocids have been reported. Polyether antibiotics present a formidable challenge for synthetic chemists; lasalocid A has ten chiral centers on the carbon backbone. We would like to report the first total synthesis of lasalocid A (**1**) with regio- and stereocontrol.

(4E,8E)-Ethyl 2-methyl-4,8-diethyldecadienoate (**2**)[7] (bp 88–90 °C (0.17 mmHg); ^{1}H NMR (CDCl$_3$) δ 5.12 (1 H, t, J = 7 Hz), 5.17 (1 H, q, J = 7 Hz)), readily synthesized by adapting Johnson's method,[8] was converted to the aldehyde **3**[7] (bp 83–85 °C (0.22 mmHg); ^{1}H NMR (CDCl$_3$) δ 5.10 (1 H, t, J = 7 Hz), 5.14 (1 H, q, J = 7 Hz), 9.59 (1 H, d, J = 2 Hz)) in 95% yield by two steps: (1) LiAlH$_4$/Et$_2$O, room temperature; (2) pyridinium chlorochromate/CH$_2$Cl$_2$, room temperature.[9] Treatment of **3** with *p*-methoxyphenylmag-

2, X = CO$_2$Et
3, X = CHO

4, X = Y = O (ketone)
5, X = H; Y = OH

6

7
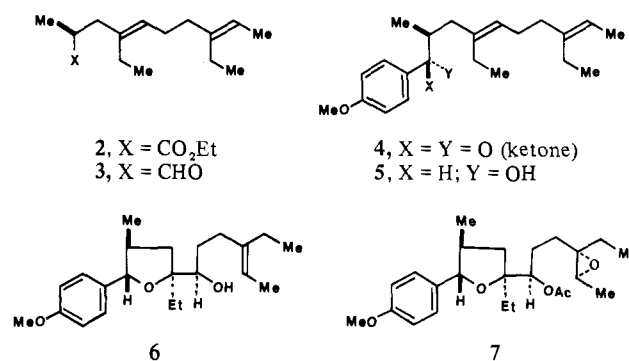
nesium bromide in ether, followed by Jones oxidation, gave the ketone **4**[7] (oil; ^{1}H NMR (CDCl$_3$) δ 5.06 (1 H, t, J = 7 Hz), 5.10 (1 H, q, J = 7 Hz)) in 72% overall yield. Highly stereospecific reduction of **4** to the alcohol **5**[7] (oil; ^{1}H NMR (CDCl$_3$) δ 4.36 (1 H, d, J = 7 Hz), 5.10 (1 H, t, J = 7 Hz), 5.13 (1 H, q, J = 7 Hz)) was realized by a combination of lithium aluminum hydride and *dl*-2-(*o*-toluidinomethyl)pyrrolidine.[10] Assignment of the stereochemistry of **5** was made based on Cram's rule.[11] The ratio of **5** and its diastereomer obtained by this method was at least 10:1 (97% yield), whereas other reducing reagents including hindered borohydrides gave less satisfactory results.[12] Optical resolution of **5** was achieved by preparative HLC separation of the *l*-α-methylbenzylurethane derivative of **5**.[13]

Epoxidation of the levorotatory alcohol **5** (*t*-BuOOH/VO-(acac)$_2$/NaOAc/C$_6$H$_6$, room temperature[14]), followed by acetic acid workup, gave the tetrahydrofuran **6**[7] (75% yield; oil; ^{1}H NMR (CDCl$_3$) δ 3.65 (1 H, br), 4.30 (1 H, d, J = 9 Hz), 5.20 (1 H, q, J = 7 Hz)) along with a small amount of its stereoisomer in a ratio of 8:1.[15] As the C-15[16] hydroxy group was expected to control the stereochemistry of the epoxidation reaction,[15] structure **6** was assigned to the major product. Repetition of epoxidation of **6** under the same conditions, followed by acetylation (Ac$_2$O/Py, room temperature),[17] allowed isolation of the epoxide **7**[7] (oil; ^{1}H NMR (CDCl$_3$) δ 2.82 (1 H, q, J = 6 Hz), 4.25 (1 H, d, J = 9 Hz), 5.03 (1 H, br)), which was transformed to the tetrahydrofuran **8**[7] (oil; ^{1}H NMR (CDCl$_3$) δ 3.72 (1 H, q, J = 7 Hz), 4.08 (1 H, m), 4.28 (1 H, d, J = 10 Hz); [α]^{22}$_D$ + 1.74° (*c* 1.44, CHCl$_3$)) by four steps ((1) 0.1 N H$_2$SO$_4$/aqueous acetone, room temperature;[18] (2) TsCl/Py, room temperature; (3) K$_2$CO$_3$/CH$_3$OH, room temperature; (4) AcOH, room temperature) in 45% overall yield. The first three steps were necessary to invert the stereochemistry of the epoxide ring. The overall stereoselectivity