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CATENATED NITROGEN LIGANDS PART I.[1] TRANSITION METAL DERIVATIVES OF TRIAZENES, TETRAZENES, TETRAZADIENES, AND PENTAZADIENES

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I. Introduction

Although the great strength of the nitrogen–nitrogen triple bond relative to the corresponding double and single bonds (946 vs. 418 and 160 kJ, respectively) strongly militates against the stability of molecules containing catenated nitrogen systems, a substantial number of such structures are in fact known. These range from 3-nitrogen systems such as the azide anion (N_3^-) and 1,3-disubstituted triazenes ($RN{=}N{-}NHR$) through 4-, 5-, 6-, and 7- to 8- and, in one instance, 10-nitrogen chains (*10*). Whereas the parent "hydronitrogens" are generally unknown or, at best, dangerously explosive, their substituted analogues frequently enjoy much greater stability, particularly when aryl substituents are present. The very extensive chemistry of these catenated nitrogen systems, which originated with Peter Griess' discovery of 1,3-diaryltriazenes in 1859 (*91*), has recently been comprehensively reported in F. A. Benson's book *The High Nitrogen Compounds* (*10*).

The coordination of catenated nitrogen ligands to transition metals also dates back to the early work of Griess (*89, 90*), which included references to copper and silver derivatives of 1,3-diphenyltriazene. Around the turn of the century Meldola and Streatfeild (*146–148*), Meunier (*150–152*), Niementowski and Roszkowski (*159*), Cuisa and Pestalozza (*55, 56*), and others reported extensively on triazene complexes of copper, silver, and mercury, and in the late 1930s and early 1940s Dwyer and colleagues (*69–74*) extended this work to include derivatives of nickel and palladium. However, most work on the coordination chemistry of triazenes and other catenated

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nitrogen ligands has been reported in the past 25 years and the field appears ripe for continued rapid growth.

The observation that, with a few notable exceptions, coordination to transition metals imparts stability to catenated nitrogen systems promises exciting developments in the future. Although organic molecules containing up to 10 linked nitrogen atoms have been synthesized, metal complexes are known to date only for systems containing 2-, 3-, 4-, or 5-nitrogen chains. The chemistry of two-nitrogen ligands—notably hydrazines, diazenes, and, of course, dinitrogen itself—has received an enormous boost in recent years from the work on nitrogen fixation. However, the exciting developments in this field have recently been extensively reviewed elsewhere (*101*) and are therefore omitted from the present article. The three-nitrogen systems include, in addition to the azide anion, triazenes, and their *N*-oxides. The chemistry of azide complexes, a large field meriting a review in its own right, is specifically excluded from the present article. Complexes of triazene *N*-oxides are also excluded since they were recently covered in an exhaustive review containing over 200 references (*68*). However complexes containing ArN=N—N(Ar)C(O) or "phosphazide" (ArN=N—N=PR_3) ligands are covered. The chemistry of four-nitrogen ligands is dominated by complexes of tetrazadienes, RN=N—N=NR, which are covered in the present article together with the few isolated examples of tetrazene derivatives. The latter include a binuclear tungsten derivative of the hypothetical *iso*-tetrazene molecule $(H_2N)_2N{=}N$. Finally, we include the first transition metal derivatives of pentazadienes RN=N—N(H)—N=NR.

Cyclic catenated nitrogen ligands will be covered in Section II.

II. Triazenide Complexes

1,3-Diaryltriazenes, the first organic compounds containing three or more nitrogen atoms in sequence, were prepared by Griess in 1859 (*91*). The less stable alkylaryl and dialkyl triazenes were first obtained by Dimroth in 1903 (*60*) and 1906 (*63*), respectively. The extremely unstable parent molecule, $HN{=}N{-}NH_2$, is formed during electrode-less discharge in a high-speed stream of hydrazine (*83*), and is also considered to be present in aqueous hydrazine solution after pulse radiolysis (*100*). However, the conjugate base, $HN{=}N{-}NH^-$, has been stabilized as a ligand in the osmium cluster $[Os_3(\mu\text{-H})(\mu\text{-HNNNH})(CO)_{10}]$ (*113*). Reviews of triazene chemistry include articles on triazene structures and stability by Süling (*204*) and Smith (*202*), diaryltriazenes by Campbell and Day (*28*), and monoalkylmonoaryltriazenes by Vaughan and Stevens (*221*).

Although the ability of triazenes to complex transition metal ions, notably copper, silver, and mercury, was recognized at a very early stage, and was further explored by Dwyer in the 1940s, most of the work in this field has been reported since 1965. Papers published between 1965 and 1974 by Corbett and Hoskins (*47–50*), Knoth (*120*), Robinson and Uttley (*190, 191*), and Brinckman *et al.* (*17*) on triazenide complexes of the group VIII metals aroused new interest in the field. Subsequent reports by many authors describe triazenide complexes of these and most other *d*-block transition metals. Numerous examples of metal complexes containing monodentate, chelate, or bridging triazenide ligands are now known. In contrast no complexes containing the fully saturated triazanes $R_2N—N(R)—NR_2$ appear to have been reported.

A. SYNTHESIS AND PROPERTIES

Diaryl-, alkylaryl-, and, to a lesser degree, dialkyltriazenes are readily available. Consequently most triazenide complexes are synthesized from the free triazene or one of its salts. The salient methods, together with illustrative examples, are given below.

1. From metal halides and free triazenes in the presence of base (*71*).

$$\mathrm{CuCl + ArNNNHAr + NaOH + 2py \longrightarrow Cu(ArNNNAr)(py)_2 + NaCl + H_2O (py, pyridine)} \quad (1)$$

2. From metal carboxylates and free triazenes (*71, 111*).

$$\mathrm{Cu(O_2CMe)_2 + 2ArNNNHAr \longrightarrow Cu(ArNNNAr)_2 + 2MeCO_2H} \quad (2)$$

$$\mathrm{[Pd(allyl)(O_2CMe)]_2 + 2ArNNNHAr \longrightarrow [Pd(allyl)(ArNNNAr)]_2 + 2MeCO_2H} \quad (3)$$

3. From metal halides and lithium (*120*), sodium (*42*), or magnesium (*17*) triazenides.

$$\mathrm{RhCl(PPh_3)_3 + LiBu^n + ArNNNHAr \longrightarrow Rh(ArNNNAr)(PPh_3)_2 + LiCl + C_4H_{10} + PPh_3} \quad (4)$$

$$\mathrm{[RhCl(CO)_2]_2 + 2Na(ArNNNAr) \longrightarrow [Rh(ArNNNAr)(CO)_2]_2 + 2NaCl} \quad (5)$$

$$\mathrm{TiCl_4 + 4(MeNNNMe)MgI \longrightarrow Ti(MeNNNMe)_4 + 4MgICl} \quad (6)$$

4. From metal halides and organosilicon or tin triazenides (*1*).

$$\mathrm{Me_3Si(ArNNNAr) + MnBr(CO)_5 \longrightarrow Mn(ArNNNAr)(CO)_4 + CO + SiBrMe_3} \quad (7)$$

$$\mathrm{Me_3Sn(ArNNNAr) + MoCl(C_5H_5)(CO)_3 \longrightarrow CO + Mo(ArNNNAr)(C_5H_5)(CO)_2 + SnClMe_3} \quad (8)$$

5. By oxidative addition of triazenes to low oxidation state metal complexes (*135*).

$$\mathrm{Ru(CO)_3(PPh_3)_2 + ArNNNHAr \longrightarrow RuH(ArNNNAr)(CO)(PPh_3)_2 + 2CO} \quad (9)$$

6. From metal hydrides (*133*) or alkyls (*53*) and free triazenes.

$$\mathrm{OsH_4(PPh_3)_3 + ArNNNHAr \longrightarrow OsH_3(ArNNNAr)(PPh_3)_2 + H_2 + PPh_3} \quad (10)$$

$$\mathrm{Li_4[Cr_2Me_8] + 4ArNNNHAr \longrightarrow Cr_2(ArNNNAr)_4 + 4CH_4 + 4LiMe} \quad (11)$$

7. From metal hydrides (*113*) or alkyls (*40*) and aryl or silyl azides.

$$\mathrm{Os_3H_2(CO)_{10} + Me_3SiN_3 \longrightarrow Os_3H(HNNNH)(CO)_{10} + SiHMe_3} \quad (12)$$

$$\mathrm{ZrMe_2(C_5H_5)_2 + PhN_3 \longrightarrow ZrMe(PhNNNMe)(C_5H_5)_2} \quad (13)$$

8. From arylamines, isoamyl nitrite, and metal acetates or nitrates (*225*).

$$\mathrm{4ArNH_2 + 2RONO + Hg(O_2CMe)_2 \longrightarrow Hg(ArNNNAr)_2 + 2MeCO_2H + 2ROH + 2H_2O} \quad (14)$$

9. From metal nitrites and aromatic amines (*159*).

$$\mathrm{AgNO_2 + 2PhNH_2 \longrightarrow Ag(PhNNNPh) + 2H_2O} \quad (15)$$

10. From metallic mercury and free triazenes in the presence of oxygen (*231*).

$$\mathrm{2Hg + 4ArNNNHAr + O_2 \longrightarrow 2Hg(ArNNNAr)_2 + 2H_2O} \quad (16)$$

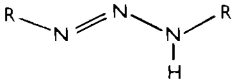
Finally, copper(I), silver(I), and mercury(II) triazenides react with selected rhodium(I), iridium(I), and platinum(II) halide complexes to afford metal–metal bonded binuclear triazenide-bridged species (*129*).

$$\mathrm{IrCl(CO)(PPh_3)_2 + Ag(ArNNNAr) \longrightarrow (PPh_3)_2(CO)Ir(\mu\text{-}ArNNNAr)AgCl} \quad (17)$$

Most triazenide complexes of the transition metals are air-stable, crystalline solids, soluble in many common nonpolar organic solvents. Most are deeply colored, ranging from bright yellow to deep red or brown. Dialkyl triazenide complexes tend to be rather less stable and those of titanium and zirconium are reported to be sensitive to air and moisture (*17*).

B. STRUCTURAL PROPERTIES

The free triazenes, RN=N—NHR, are generally believed to adopt a trans configuration (**1**) and this arrangement has been confirmed for several diaryltriazenes by X-ray diffraction studies (*122*, *123*, *163*). No examples of salts containing noncoordinated triazenide anions appear to have been characterized by X-ray diffraction methods. The triazenide anions, RN=N—NR$^-$, are formally analogous to the nitrite anion, O=N—O$^-$, and might be expected to display a similar variety of coordination modes. The most feasible of these are illustrated in formulas **2**–**8**. Numerous examples of complexes containing monodentate (**2**), chelate (**3**), or bridging (**4**) triazenide ligands have been reported. The N-1,N-1- and N-1,N-2-bridging arrangements (**5** and **6**) have not been observed, and coordination through N-2 (**7**)—analogous to that found in the nitro form of NO_2^- coordination—is also unknown. Finally the η^3-structure (**8**), which is formally related to that found in η^3-allyl complexes, is still only a hypothetical bonding option.



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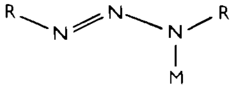

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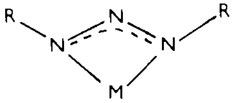

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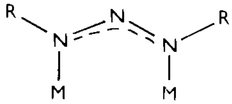

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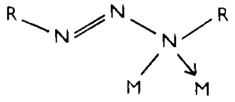

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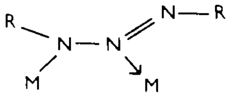

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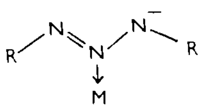

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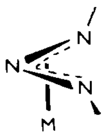


(8)

1. Monodentate Triazenide Structures

Although monodentate triazenide ligands were first proposed (erroneously) by Meunier in 1900 (*150, 152*) for the copper(I) complex "Cu(PhNNNPh)," this mode of coordination was not finally confirmed until 1976 when Brown and Ibers (*21, 22*) reported the X-ray crystal structure of *cis*-Pt(PhNNNPh)$_2$(PPh$_3$)$_2$·C$_6$H$_6$ (Fig. 1). Monodentate triazenide ligands remain relatively rare and are mainly confined at present to the four-coordinate d^8 metal ions, Rh(I), Ir(I), Pd(II), and Pt(II). To date only six examples have been characterized by diffraction methods (see Table I). In some of these, notably *trans*-PtH(*p*-tol-NNN-tol-*p*)(PPh$_3$)$_2$, there is a short nonbonded contact (2.91 Å) between the metal and the terminal (N-3) nitrogen atom (*109*). Variable-temperature proton NMR studies (see Section II,C,3) have established that η^1-triazenide ligands, like their η^1-allyl counterparts, display fluxional behavior.

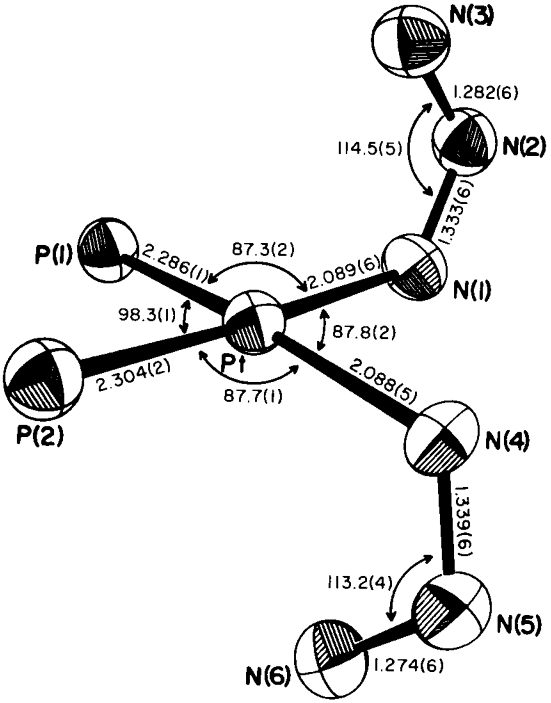


FIG. 1. View of the environment of the platinum atom in *cis*-Pt(PhNNNPh)$_2$(PPh$_3$)$_2$ showing salient bond lengths and angles.

2. *Chelate Triazenide Structures*

Chelate structures in which the triazenide anion coordinates to the metal through nitrogens N-1 and N-3 were first advanced by Dwyer in 1939 for silver(I) and mercury(II) triazenide complexes (*69*, *70*), and subsequently for nickel(II) and palladium(II) derivatives (*71*, *74*). This proposal was at first criticized by Sidgwick (*199*) and others (*98*), who reasoned that closure of four-membered chelate rings in triazenide or carboxylate complexes would impose excessive steric strain. Although Dwyer's ideas were later vindicated, some of his original structures were incorrect, and it was not until 1967 that Corbett and Hoskins' X-ray crystal structure of the cobalt complex $Co(PhNNNPh)_3$ (Fig. 2) finally provided unequivocal proof that triazenide anions could serve as chelate ligands (*49*). It is interesting to note that this structure was the first in which the presence of three four-membered chelate rings within the same octahedral coordination sphere was established. Fourteen X-ray structures involving chelate triazenide ligands are listed in Table I together with salient bond lengths and angles for each. The twofold symmetry of the triazenide ligands in the tris(chelates) $M(PhNNNPh)_3$ ($M = Cr$, Co) clearly establishes the electron delocalization in the chelate triazenide ligand. The high degree of strain in the four-membered chelate rings is amply demonstrated by the angles subtended at the metal center ($\angle$N-1—M—N-3 $\sim$56–65°) and at the central nitrogen ($\angle$N-1—N-2—N-3 $\sim$99–107°).

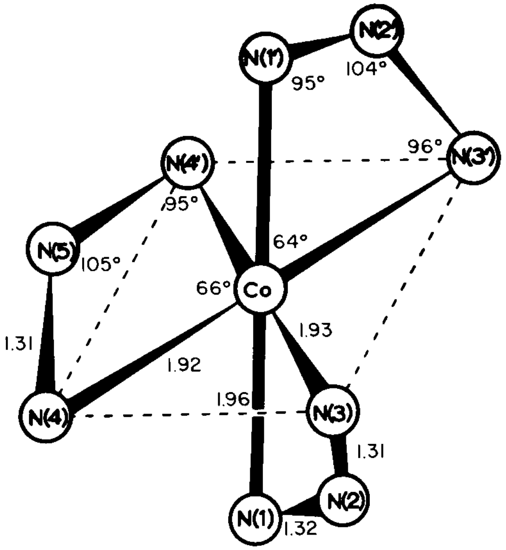
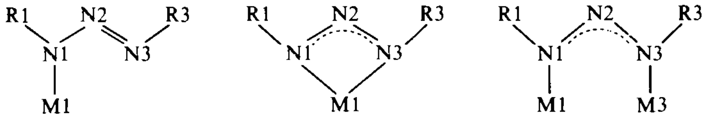


FIG. 2. View of the environment of the cobalt atom in $Co(PhNNNPh)_3$ showing salient bond lengths (in Å) and angles (in degrees).

TABLE I

Selected Bond Lengths[a, b] and Angles[a, b] for Triazenide Complexes



Molecular formula	R1	R3	M1—M3	M1—N1	M1—N3	M3—N3	N1—N2	N2—N3	∠N1M1N3	∠N1N2N3	∠M1M3N3	∠M3M1N1	References
Monodentate triazenide													
trans-Pd(RNNNR)Cl$(PPh_3)_2$	*p*-tol	*p*-tol	—	2.033	(2.836)	—	1.336	1.286	—	113.0	—	—	*12, 13, 209*
trans-Pt(RNNNR)Cl$(PPh_3)_2$	*p*-tol	*p*-tol	—	2.114	(3.008)	—	1.266	1.257	—	116.4	—	—	*12, 209*
trans-Pt(RNNNR)H$(PPh_3)_2$	*p*-tol	*p*-tol	—	2.090	(2.908)	—	1.310	1.264	—	111.6	—	—	*109, 209*
cis-Pt$(RNNNR)_2(PPh_3)_2$	Ph	Ph	—	2.088	(2.974)	—	1.336	1.278	—	113.9	—	—	*21, 22*
trans-Ir(RNNNR)(CO)$(PPh_3)_2$	*p*-tol	*p*-tol	—	2.16	(2.58)	—	1.31	1.28	—	109.7	—	—	*110*
PhHg(RNNNR)	*o*-ClC_6H_4	Ph	—	2.14	(2.46)	—	1.36	1.33	—	99	—	—	*133*
Chelate triazenide													
$Cr(RNNNR)_3$	Ph	Ph	—	2.01	2.01	—	1.31	1.31	62	105			*53*
$Mo_2(RNNNR)_2(NMe_2)_4$	*p*-tol	*p*-tol	2.212	2.271	2.231	—	1.310	1.316	55.8	106.7	—	—	*37*
Mo(RNNNR)$(C_5H_5)(CO)_2$	Ph	Ph	—	2.12		—	1.31		56	101	—	—	*179*
Mo(RNNNR)$(C_5H_5)(CO)_2$	$C_6H_3(CF_3)_2$	$C_6H_3(CF_3)_2$	—	2.114	2.126	—	1.326	1.292	56.8	100.8	—	—	*182*
$W_2(RNNNR)_2(NMe)_2Et_2$	Ph	Ph	2.304	2.232	2.160	—	1.308	1.325	56.68	104.8	—	—	*35a*
$W_2(RNNNR)_2(NMe_2)_4$	Ph	Ph	2.314	2.186	2.211	—	1.32		56.6	104.5	—	—	*39*
Tc(RNNNR)$(CO)_2(PMe_2Ph)_2$	*p*-tol	*p*-tol	—	2.186		—	1.316		57.2	105.4	—	—	*142a*
Re(RNNNR)$(CO)_2(PPh_3)_2$	Ph	Ph	—	2.21	2.18	—	1.33	1.31	57	105	—	—	*87*
Re(RNNNR)$Cl_2(PPh_3)_2$	*p*-tol	*p*-tol	—	2.08	1.99	—	1.31	1.30	58	99	—	—	*192*
Ru(RNNNR)H(CO)$(PPh_3)_2$	*p*-tol	*p*-tol	—	2.149	2.179	—	1.318	1.310	57.7	105.2	—	—	*20, 22*
$Co(RNNNR)_3$ (monoclinic)	Ph	Ph	—	1.94		—	1.31		65	105	—	—	*49*
$Co(RNNNR)_3$ (trigonal)	Ph	Ph	—	1.92		—	1.31		64.8	103.2	—	—	*127*
$(OC)_5MnHg(RNNNR)$	*p*-ClC_6H_4	*p*-ClC_6H_4	2.557	2.314	2.435	—	1.332	1.262	52.82	109.2	—	—	*112*
$W(PhNNNPPh_3)Br_2(CO)_3$[c]	Ph	PPh_3	—	2.163	2.220	—	1.279	1.364	56.7	103.8	—	—	*105*
$[(C_8H_{12})Ir(RNNNR)_2HgCl]_2$[d]	*p*-tol	*p*-tol	—	2.19	2.06	—	1.30	1.29	58.2	106	—	—	*217*

Bridging triazenide													
$Cr_2(RNNNR)_4$	Ph	Ph	1.858	2.052	—	2.037	1.297	1.302	—	112.8	93.2	94.2	*53*
$Mo_2(RNNNR)_4$	Ph	Ph	2.083	2.145	—	2.13	1.33	1.30	—	113	91.4	91.4	*53*
$Mo_2(RNNNR)_2(NMe_2)_2Me_2$	*p*-tol	*p*-tol	2.174	2.283	—	2.157	1.290	1.134	—	113.1	86.1	91.7	*38*
$Mo_2(RNNNR)_2(NMe_2)_2Et_2$	*p*-tol	*p*-tol	2.171	2.205	—	2.212	1.283	1.315	—	113.7	89.3	89.3	*34*
$W_2(RNNNR)_2(NMe_2)_2Et_2$	*p*-tol	*p*-tol	2.267	2.156	—	2.254	1.305	1.316	—	—	—	—	*35a*
$W_2(RNNNR)_2(dmhp)_2$	Ph	Ph	2.169	2.108	—	2.097	1.33	1.33	—	111.9	90.6	90.1	*52*
$Os_3(RNNNR)H(CO)_{10}$	H	H	2.923	2.12	—	2.13	1.32	1.32	—	118	—	—	*113*
$Os_3(RNNNR)H(CO)_{10}$	H	Ph	2.900	2.137		2.110	1.32	1.29	—	117.5	—	—	*26*
$Rh_2(RNNNR)_2(CO)_2(PPh_3)_2$	*p*-tol	*p*-tol	2.960	2.135	—	2.140	—	—	—	—	—	—	*43*
$[Rh_2(RNNNR)_2(CO)_2(PPh_3)_2]PF_6$	*p*-tol	*p*-tol	2.698	2.095	—	2.098	—	—	—	—	—	—	*43*
$Ni_2(RNNNR)_4$	Ph	Ph	2.395	1.924	—	1.907	1.312		—	116.5	86.8	86.4	*45, 46, 50*
$Pd_2(RNNNR)_4$	Ph	Ph	2.5626	2.049	—	2.033	1.313		—	117.6	85.0	84.9	*45, 46*
$Pd_2(RNNNR)_2(methallyl)_2$	Me	Me	(2.97)	2.115	—	2.128	1.32	1.30	—	118.3	—	—	*103*
$Pd_2(RNNNR)_2(methallyl)_2$	*p*-tol	*p*-tol	(2.86)	2.098	—	2.120	1.298	1.301	—	116.7	—	—	*29*
$Cu_2(RNNNR)_4$	Ph	Ph	2.441	2.032	—	2.007	1.296		—	117.1	85.7	85.4	*45, 46*
$Cu_2(RNNNR)_2$	Ph	Ph	2.45	1.90	—	1.94	1.27	1.32	—	115.8	86.2	86.0	*19*
$Cu_4(RNNNR)_4$	Me	Me	2.66	1.87	—	1.87	1.29		—	116.0	—	—	*161*
$Au_4(RNNNR)_4$	Ph	Ph	2.85	2.04	—	2.04	1.27	1.30	—	118.6	—	—	*6a*
$Zn_4O(RNNNR)_6$	Ph	Ph	(3.11)	2.04	—	2.04	1.31		—	117.0	—	—	*48*
$(Ph_3P)_2(CO)Rh(RNNNR)CuCl$	Me	Me	2.730	2.14	—	1.91	1.25	1.27	—	119	85.0	79.1	*124*
$(Me_2PhP)_2(CO)Ir(RNNNR)CuCl$	Me	Me	2.686	2.08	—	1.89	1.29	1.29	—	116	86.9	78.8	*125*
$(Ph_3P)_2(CO)Ir(RNNNR)AgO_2CPr^i$	Me	*p*-tol	2.874	2.086	—	2.111	1.298	1.339	—	115.1	80.6	81.3	*131*
$[(C_8H_{12})Ir(RNNNR)_2HgCl]_2$[d]	*p*-tol	*p*-tol	2.618	2.10	—	2.42	1.31	1.27	—	117	80.7	82.3	*217*

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[a] Bond lengths in angstroms (Å), angles in degrees (°). Values in parentheses refer to nonbonded distances.

[b] For complexes of high symmetry, bond lengths and angles quoted are averaged values for equivalent bonds.

[c] P—N—3 = 1.672 Å.

[d] This complex contains chelate and bridging triazenide ligands; see entries under both headings.

3. Bridging Triazenide Structures

A binuclear structure with chelating and bridging triazenide ligands was proposed by Dwyer and Mellor in 1941 (*74*) for the nickel(II) complex $Ni_2(PhNNNPh)_4$. However, this structure was incorrect and it was not until 1958 that Harris *et al.* (*98*) suggested that this complex and related copper(II) and palladium(II) derivatives all possess the now familiar copper(II) acetate or "lantern" structure (Fig. 3; M = Ni, Cu, or Pd). X-Ray diffraction studies on the nickel complex $Ni_2(PhNNNPh)_4$ (*46, 50*), the copper complex $Cu_2(PhNNNPh)_4$ (*46*), and the palladium complex $Pd_2(PhNNNPh)_4$ (*46*) subsequently established the correctness of Harris' suggestion. More recently, the same "lantern" structure has been established for $Cr_2(PhNNNPh)_4$ and $Mo_2(PhNNNPh)_4$ (*53*) by diffraction methods, and it is now recognized that the geometry of triazenide ligands is particularly suited to bridge formation in bi- or polynuclear metal complexes. Other interesting structures involving triazenide ligands include the copper(I) derivatives $Cu_2(PhNNNPh)_2$ (Fig. 4)

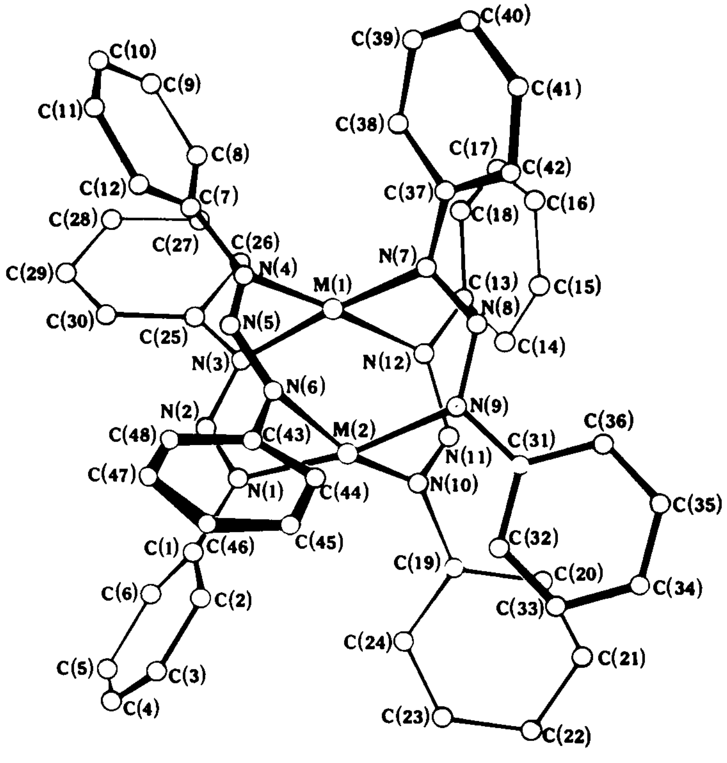


FIG. 3. View of the $M_2(PhNNNPh)_4$ dimers (M = Cu, Ni, Pd), showing the bridging of the metal atoms by the four triazenide ligands.

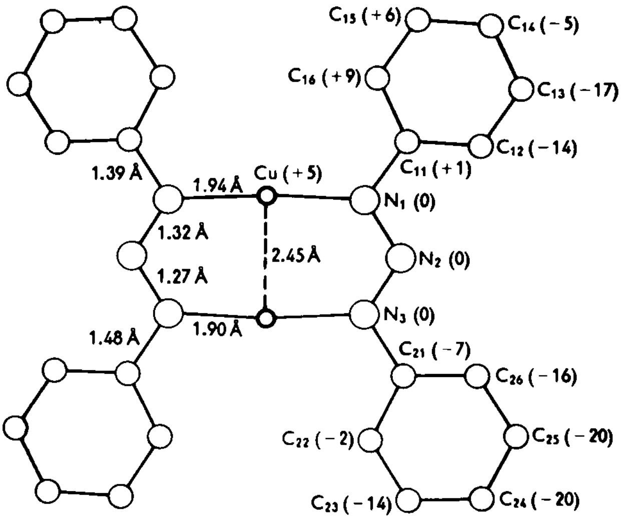


FIG. 4. Molecular structure of $[Cu(PhNNNPh)]_2$ dimers.

(*19*) and $Cu_4(MeNNNMe)_4$ (Fig. 5) (*161*), the allylpalladium complexes $Pd_2(RNNNR)_2(allyl)_2$ (*29, 103*), and the tetranuclear zinc complex $Zn_4O(PhNNNPh)_6$ (*48*), which has a "basic beryllium acetate" structure. A number of heterobinuclear complexes have been shown to contain bridging triazenide ligands supported by metal–metal bonds (see Sections II,E,5 and II,E,6). A full list of diffraction studies on triazenide complexes is given in Table I.

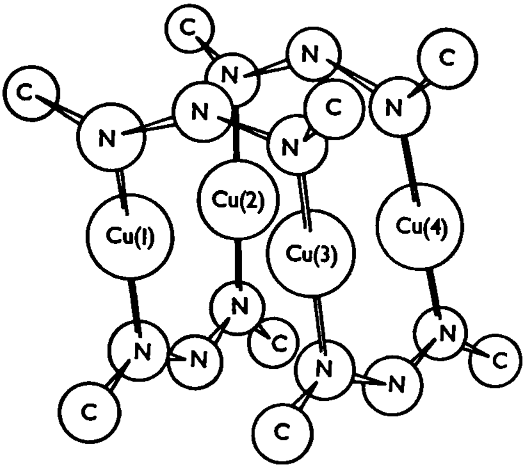


FIG. 5. Molecular structure of $[Cu(MeNNNMe)]_4$ tetramers.

C. SPECTROSCOPIC STUDIES

1. *Vibrational Spectra*

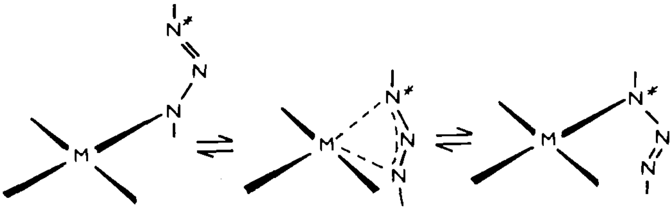
1,3-Diaryltriazenes display infrared absorptions in the range of ~1100–1600 cm^{-1}, attributable to vibrations of the $-\mathrm{N{=}N{-}N}<$ skeleton (*128*), which are perturbed on complex formation. Several authors have attempted to use these perturbations to determine the mode of coordination of the triazenide ligand. Robinson and Uttley (*190, 191*) reported that monodentate triazenide ligands absorbed at ~1150, 1190–1210, 1260–1300, and 1580–1600 cm^{-1}, whereas their chelate analogues absorbed only at 1260–1300 and 1580–1600 cm^{-1}. Knoth (*120*), in a later paper, reported that bridging triazenide ligands, in particular those in $Ni_2(PhNNNPh)_4$, show infrared spectral characteristics similar to those observed for monodentate triazenide ligands. Knoth further claimed that the complexes $M(PhNNNPh)(CO)(PPh_3)_2$ (M = Rh or Ir), which according to the criteria of Robinson and Uttley contain monodentate triazenide ligands, were really five-coordinate chelate complexes. However, this assertion was based on an erroneous interpretation of NMR data (*120*) and has subsequently been shown to be incorrect by an X-ray diffraction study of $Ir(p\text{-tol-NNN-tol-}p)(CO)(PPh_3)_2$, which has established the monodentate nature of the triazenide ligand (*110*). Kuyper *et al.* (*129, 130*) suggested that the absorptions at 1580–1600 cm^{-1} arose from the aryl groups rather than the triazenide skeleton, and further reported (*102, 129, 130*) that bridging triazenide ligands display a characteristic skeletal vibration at 1350–1375 cm^{-1}. This observation, taken with those of Robinson and Uttley, suggests that with care triazenide coordination modes can be assigned on the basis of vibrational spectra in most simple structures. However, in complex structures the situation is more ambiguous. This point is highlighted by the observation (*215*) that the triazenide skeletal vibrations for the binuclear complexes $[2,6\text{-}(Me_2NCH_2)C_6H_3](p\text{-tol-NNNR})PtAgBr$ (R = Me, Et) do not correspond to any of the categories given above.

2. *Electronic Spectra*

Studies of electronic spectra are confined almost exclusively to derivatives of d^{10} silver(I) (*236, 237*) and mercury(II) (*79, 194, 234*), both of which have been investigated extensively. Data have also been recorded for copper(II) triazenide complexes (*79, 236*) and nickel(II) (*84*).

3. *Nuclear Magnetic Resonance*

Proton NMR has been used extensively in the routine assignment of stereochemistry, particularly for triazenide ligands containing alkyl, *p*-tolyl,



SCHEME 1. 1,3-Metallotropic equilibria in η^1-triazenide complexes.

or *p*-methoxyphenyl groups (*1, 17, 102, 120, 135, 190*). Variable-temperature proton NMR has been employed to study 1,3-metallotropic equilibria in η^1-triazenide complexes (Scheme 1) (*54, 180, 191, 208, 209*). Other processes investigated by variable-temperature proton NMR include dynamic interchange of chelate and bridging triazenide ligands (*217*), and the exchange of free and coordinated triazenes (*158*). Variable-temperature $^{13}C\{^1H\}$ NMR has also been used to examine fluxional processes in triazenide complexes (*126, 158, 179, 183, 217*). Intramolecular 1,3-metallotropic-exchange reactions in phenylmercuric triazenide complexes have been studied by ^{19}F, ^{15}N, and ^{199}Hg NMR (*126, 157, 172, 174, 175*).

4. *Electron Spin Resonance*

Few triazenide complexes reported to date are paramagnetic. Examples studied by ESR are restricted to the low-spin d^5 osmium(III) complexes $OsX_2(PhNNNPh)(PPh_3)_2$ (*3*), the binuclear mixed-valence rhodium salts $[\{Rh(\mu\text{-}ArNNNAr)(CO)(PPh_3)\}_2][PF_6]$ (*43*), and the low-spin d^7 cobalt(II) species $Co(ArNNNAr)(C_5H_5)L$ (*178*).

5. *Mass Spectroscopy*

Most triazene complexes are thermally stable and, where mass spectra have been recorded, molecular ions are usually observed. Fragmentation initially involves loss of ancillary ligands, notably CO; cleavage of the diaryltriazenide ligands generates aryl, aryldiazo, and arylazo ions together with nitrene species $[L_nM{=}NAr]^+$ (*1, 42, 174, 179*).

D. CHEMICAL REACTIVITY

Triazenide ligands when bound to transition metals are very stable entities and the $-N \overset{...}{=} N \overset{...}{=} N-$ system does not fragment except under the most vigorous conditions. Reactions undergone by coordinated triazenide ligands include protonation (*44*),

$$\mathrm{Rh(ArNNNAr)(CO)(PPh_3)_2 + HBF_4} \longrightarrow \mathrm{[Rh(ArNNNHAr)(CO)(PPh_3)_2][BF_4]} \qquad (18)$$

reductive elimination (*207*, *208*),

$$\mathrm{PtH(ArNNNAr)(PPh_3)_2 + 2PPh_3} \longrightarrow \mathrm{Pt(PPh_3)_4 + ArNNNHAr} \qquad (19)$$

and carbonyl (*177*) or isocyanide (*180*) "insertion."

$$\mathrm{CoI_2(C_5H_5)(CO) + Ag(ArNNNAr)} \longrightarrow \mathrm{\overline{CoI\{ArNNN(Ar)C}(O)\}(C_5H_5) + AgI} \qquad (20)$$

$$\mathrm{Ni(ArNNNAr)(C_5H_5)(CNR)} \longrightarrow \mathrm{\overline{Ni\{ArNNN(Ar)C}(NR)\}(C_5H_5)} \qquad (21)$$

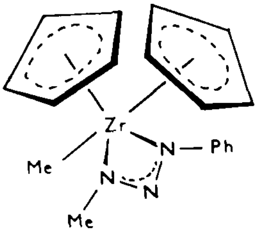
Electrochemical redox reactions have been reported for triazenide complexes of iron (*214*), cobalt (*214*), and rhodium (*43*).

E. GROUP SURVEY

To date no triazenide complexes appear to have been reported for the scandium, yttrium, and lanthanum group of metals.

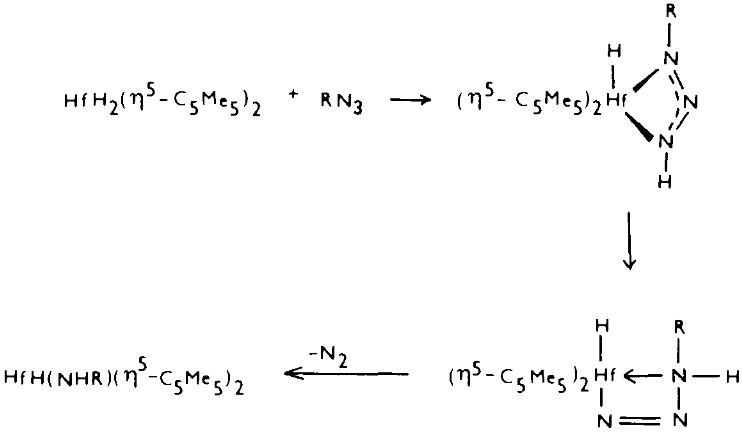
1. Titanium, Zirconium, and Hafnium

Titanium and zirconium tetrahalides react with dimethyltriazenide-magnesium iodide, prepared from MeMgI and $\mathrm{MeN_3}$, to afford the volatile, moisture-sensitive dark red (M = Ti) or orange (M = Zr) complexes $\mathrm{M(MeNNNMe)_4}$. Proton NMR data (δ_{Me} single sharp peak) are consistent with symmetrical tetrakis(chelate) structures for both complexes (*17*). Treatment of the same tetrahalides with Ag(PhNNNPh) under anhydrous conditions yields $\mathrm{TiCl(PhNNNPh)_3}$ and $\mathrm{Zr(PhNNNPh)_4}$ (*18*). The organozirconium complex $\mathrm{ZrMe_2(C_5H_5)_2}$ reacts with $\mathrm{Me_3SiN_3}$ to produce the azide complex $\mathrm{Zr(N_3)Me(C_5H_5)_2}$ but with phenyl azide affords a yellow air-sensitive triazenide derivative $\mathrm{Zr(MeNNNPh)Me(C_5H_5)_2}$, for which a chelate structure (**9**) has been proposed (*40*). The analogous complex $\mathrm{Zr(PhNNNPh)Ph(C_5H_5)_2}$ was prepared in a similar fashion (*40*). Triazenide complexes have been implicated as reactive intermediates in the formation of hafnium amides from azides and hafnium hydrides (Scheme 2) (*106*). Nitrogen-15 NMR-labeling experiments confirm that the terminal nitrogen of the azide formally inserts into the Hf—H bond. Isolation of diamides $\mathrm{Hf(NHR)_2(C_5Me_5)_2}$ as the sole products when excess azide, $\mathrm{RN_3}$, is used has tentatively been attributed to the formation and subsequent decomposition of the



(9)

unstable η^1-triazenides $Hf(HNNNR)_2(C_5Me_5)_2$ and $Hf(NHR)(HNNNR)(C_5Me_5)_2$ (*106*). Species of this type, notably $HfH(HNNNAr)(C_5Me_5)_2$ and $HfH(ArNNNAr)(C_5Me_5)_2$ have been obtained from reactions of $HfH_2(C_5Me_5)_2$ with azides (ArN_3) and triazenes (ArNNNHAr), respectively (*106*).



SCHEME 2. Pathways for the formation of the hafnium amides from azides and hafnium hydrides. Reprinted with permission from *Organometallics* **1**, 1025. Copyright (1982) American Chemical Society.

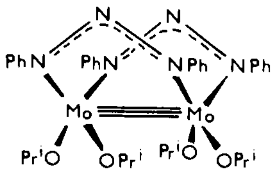
To date no triazenide complexes have been reported for the vanadium, niobium, and tantalum triad of elements.

2. *Chromium, Molybdenum, and Tungsten*

The complex anion $[Cr(PhNNNPh)(CO)_4]^-$, prepared from $Cr(CO)_6$ and Na[PhNNNPh], has been isolated as an orange tetramethylammonium salt (*118*). Stoichiometric reactions of $CrPh_3(THF)_3$ with diphenyltriazene in tetrahydrofuran (THF) solution afford the triazenide chelates $CrPh_2(PhNNNPh)(THF)_2$, $CrPh(PhNNNPh)_2(THF)$, and $Cr(PhNNNPh)_3$. Thermal and hydrolytic stability increases with increasing triazene content (*195*). The tris(chelate) $Cr(PhNNNPh)_3$ has also been obtained as the major product from the reaction of $[Cr_2Me_8]^{4-}$ with diphenyltriazene, and has been shown to possess a severely strained octahedral structure (*53*). The minor product of this reaction, $Cr_2(PhNNNPh)_4$, has been found to possess the expected "lantern" structure (Fig. 3, M = Cr), analogous to that found for chromium(II) acetate (*53*). However, there is considerable torsional rotation away from a perfectly eclipsed structure and the chromium-chromium distance [1.858(1) Å] is extremely short even for a quadruple bond [cf. 2.362(1) Å for chromous acetate (*51*)].

The analogous molybdenum complex, obtained from $[Mo_2Me_8]^{4-}$ and diphenyltriazene, has a similar "lantern" structure [$Mo{\equiv}Mo$ 2.083(2) Å] (*53*). Binuclear molybdenum(II) triazenide complexes $Mo_2(ArNNNAr)_4$ (Ar = Ph, *p*-tol) have also been obtained from the organomolybdenum(II) species $Mo_2R_2(NMe_2)_4$ (R = Et, Pr^i, Bu^n, Bu^s, Bu^t, or Bz) (*34*, *35*), and a "lantern" structure has been confirmed for Mo_2(*p*-tol-NNN-tol-*p*)$_4$ (*34*). However, with closely related precursors $Mo_2R_2(NMe_2)_4$ (R = Me or CH_2SiMe_3) substitution is incomplete and the dialkyl products $Mo_2R_2(NMe_2)_2(ArNNNAr)_2$ are obtained (*34*). The dimethyl complex $Mo_2Me_2(NMe_2)_2$(*p*-tol-NNN-tol-*p*)$_2$ (*38*) and its diethyl analogue $Mo_2Et_2(NMe_2)_2$(*p*-tol-NNN-tol-*p*)$_2$, isolated as an intermediate from the reaction of $Mo_2Et_2(NMe_2)_4$ with di-*p*-tolyltriazene (*34*), have been shown to possess a pair of molybdenum atoms [$Mo{\equiv}Mo$ 2.174(1) and 2.171(4) Å, respectively] bridged by a *cis* pair of triazenide ligands (Fig. 6). A similar structure (**10**) has been proposed on the basis of ^1H NMR data for the complex $Mo_2(OPr^i)_4(PhNNNPh)_2$ isolated from the reaction of $Mo_2(OPr^i)_6$ and diphenyltriazene (*36*). However, the closely related complex $Mo_2(NMe_2)_4$(*p*-tol-NNN-tol-*p*)$_2$, obtained from $Mo_2(NMe_2)_6$ and the free triazene, adopts a rather different structure (Fig. 7), with chelate triazenide ligands and an unsupported molybdenum-molybdenum triple bond [2.212(1) Å] (*37*).

A range of mononuclear molybdenum complexes containing chelate triazenide ligands has also been reported. The orange anion



(10)

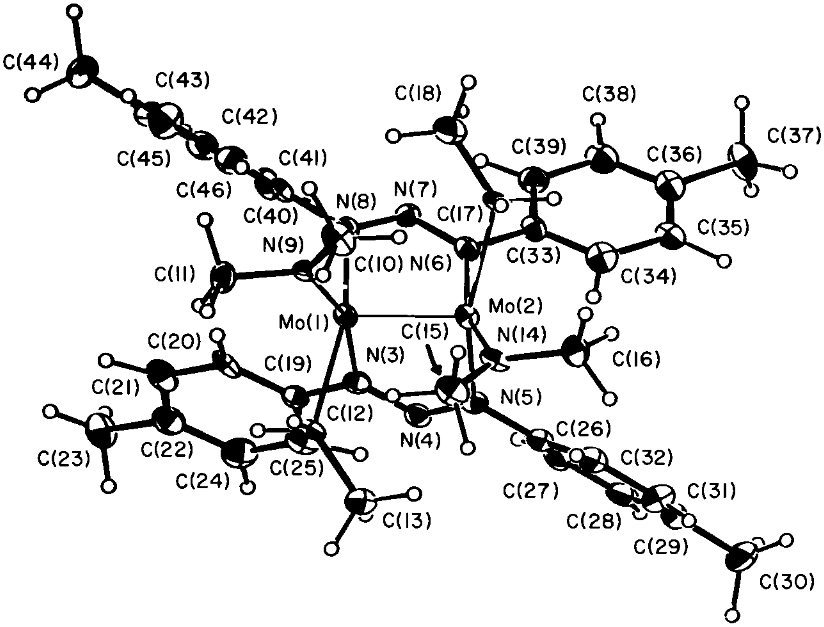


FIG. 6. An ORTEP view of the $Mo_2Et_2(NMe_2)_2$(*p*-tol-NNN-tol-*p*)$_2$ molecule.

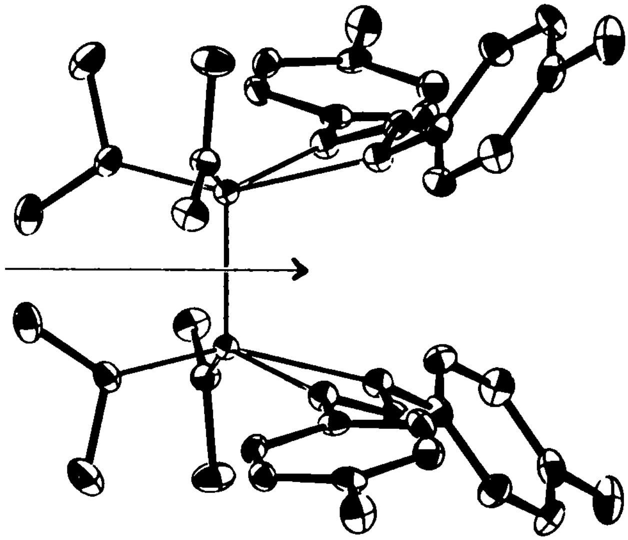
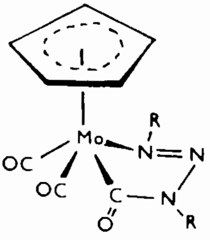


FIG. 7. An ORTEP view of the $Mo_2(NMe_2)_4$(*p*-tol-NNN-tol-*p*)$_2$ molecule.

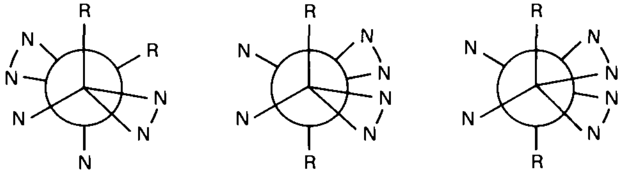
$[Mo(PhNNNPh)(CO)_4]^-$, prepared from $Mo(CO)_6$ and Na[PhNNNPh] in boiling 1,2-dimethoxyethane, can be isolated as its tetramethylammonium salt (*118*). The complexes $Mo(ArNNNAr)(C_5H_5)(CO)_2$ have been obtained from $MoCl(C_5H_5)(CO)_3$ and Na- or K[PhNNNPh] (*58, 118*), $ArNNNAr{\cdot}SnMe_3$ (*1*), Ag(ArNNNAr) (*179*), or ArNNNHAr/py (*117*). A carbonyl "insertion" product (**11**) has also been isolated from the reaction of



(11)

$MoCl(C_5H_5)(CO)_3$ with K[PhNNNPh] (*58*). An X-ray diffraction study has established a "piano stool" structure with a symmetrically bound triazenide ligand for the complex $Mo(ArNNNAr)(C_5H_5)(CO)_2$ [Ar = $3{,}5\text{-}C_6H_3(CF_3)_2$] (*182*). However, variable-temperature ^{13}C NMR spectra reveal that for derivatives of nonsymmetric diaryltriazenes, Mo(ArNNNR)$(C_5H_5)(CO)_2$, a fluxional process involving interchange of the two carbonyl ligands via a Berry-type pseudo-rotation is operative when R = aryl but not when R = alkyl (*179*). In contrast, the nitrosyl complexes $MoX(NO)(ArNNNAr)(C_5H_5)$, obtained from the dimers $[MoX_2(NO)(C_5H_5)]_2$ and Ag(ArNNNAr) (X = Cl, Br, I) (*181*) or PhNNNHPh (X = I) (*118*), are nonfluxional on the NMR timescale (*181*). Attempts to replace the halides X by neutral ligands (CO, PR_3, etc.) in the presence of $AgPF_6$ or $TlPF_6$ were unsuccessful (*181*). A "phosphazide" structure similar to that established for the tungsten analogue (see below) has been assigned to the complexes $MoBr_2(CO)_3(ArNNNPPh_3)$, obtained from the aryl azides ArN_3 (Ar = Ph, *p*-tol) and $MoBr_2(CO)_3(PPh_3)_2$ (*105*).

The binuclear tungsten complexes $W_2(NMe_2)_4(PhNNNPh)_2$ (*39*) and $W_2Bz_2(NMe_2)_2(PhNNNPh)_2$ (*35*) have been obtained from the reaction of diphenyltriazene with $W_2(NMe_2)_6$ and $W_2Bz_2(NMe_2)_4$, respectively. The first of these has a binuclear structure with chelate triazenide ligands and an unsupported W≡W bond [2.314(1) Å] (*39*), similar to that found for the molybdenum analogue (*37*). The second is assigned a triazenide-bridged structure (*35*) similar to that found for the molybdenum complex $Mo_2Me_2(NMe_2)_2(p\text{-tol-NNN-tol-}p)_2$ (Fig. 6). *Anti* and *gauche* forms of $W_2Et_2(NMe_2)_4$ react with diaryltriazenes ArNNNHAr (Ar = Ph or *p*-tol) to



isomer A isomer B isomer C

(12)

give three isomers of $W_2Et_2(NMe_2)_2(ArNNNAr)_2$ (**12a,b,c**). With time, isomer **12a** is converted to **12b** which reacts further to give an equilibrium mixture of **12b** and **12c**. Triazenide chelated and bridged structures have been confirmed for **12b** (Ar = Ph) and **12c** (Ar = *p*-tol) by diffraction methods (*35a*). The mixed ligand complex $W_2(PhNNNPh)_2(dmhp)_2$ (dmhpH=2,4-dimethyl-6-hydroxypyrimidine), obtained from $W_2(dmhp)_4$ and Li(PhNNNPh), has a "lantern" structure with a transoid arrangement of bridging triazenide ligands and a tungsten–tungsten distance of 2.169(1) Å (*52*). Several mononuclear tungsten triazenide complexes have been described. Tungsten hexacarbonyl and sodium diphenyltriazenide afford the orange anion $[W(PhNNNPh)(CO)_4]^-$, which is isolable as an air-stable orange tetramethylammonium salt (*118*). The complexes $W(ArNNNAr)(C_5H_5)(CO)_2$, obtained from $WCl(C_5H_5)(CO)_3$ and potassium (*58*) or silver triazenides, display fluxional behavior similar to that of their molybdenum analogues (*179*). Irradiation of $WCl(C_5H_5)(CO)_3$/PhNNNHPh/py mixtures affords the same product (*117*). The tungsten monoaryl triazenide W(HNNN-tol-*p*)(CO)(NO)$(PPh_3)_2$ has been obtained from $WH(CO)_2(NO)(PPh_3)_2$ and *p*-tolyl azide (*107*). Finally, infrared and NMR studies [$\delta_{PPh} = 42.0$ ppm, no *J*(PW) coupling] support a novel "phosphazide" structure for the product obtained from *p*-tolyl azide and $WBr_2(CO)_3(PPh_3)_2$ (*107*), and this assignment has subsequently been confirmed by X-ray diffraction (Fig. 8) (*105*).

3. Manganese, Technetium, and Rhenium

Manganese pentacarbonyl bromide reacts with Na[PhNNNPh] (*118*), $ArNNNAr{\cdot}SiMe_3$ (*1*), or $ArNNNAr{\cdot}SnMe_3$ (*1*) to generate the chelate complexes $Mn(ArNNNAr)(CO)_4$, which in turn readily lose a carbonyl ligand to form monosubstituted products $Mn(ArNNNAr)(CO)_3L$ (L = PPh_3, PMe_2Ph, and $AsPh_3$) (*1*).

The first technetium triazenide complexes $Tc(ArNNNAr)(CO)_2(PR_2Ph)_2$ (R = Me, Ph) have been prepared from Li(ArNNNAr) and $TcCl(CO)_2(PMe_2Ph)_3$ or $TcCl(CO)_3(PPh_3)_2$ in boiling benzene. The di-*p*-tolyltriazenide derivative Tc(*p*-tol-NNN-tol-*p*)$(CO)_2(PMe_2Ph)_2$ has been

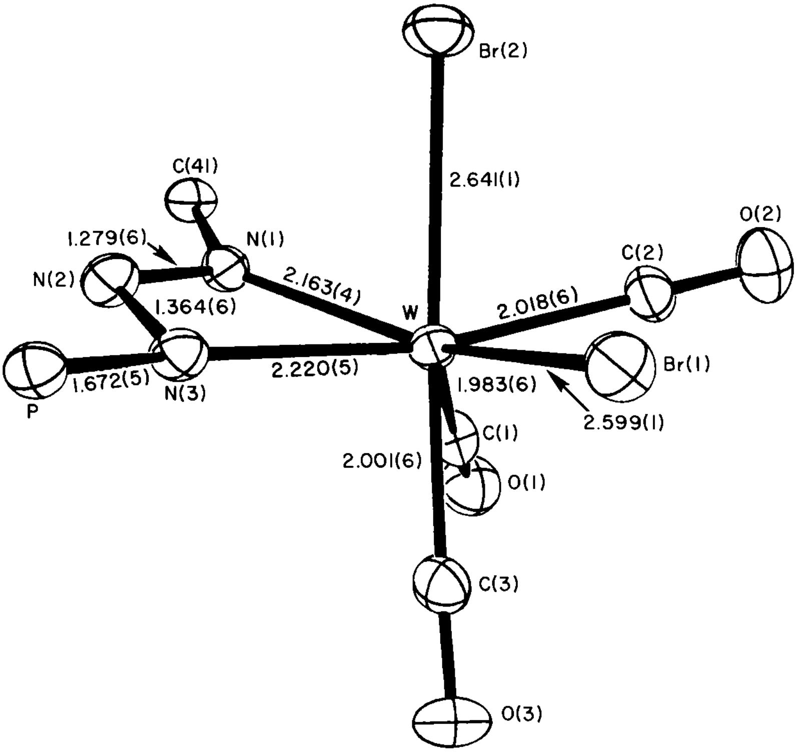


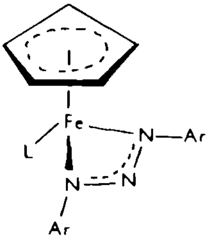
FIG. 8. View of the environment of the tungsten atom in $WBr_2(CO)_3$(*p*-tol-NNN-PPh_3).

shown to possess a distorted octahedral structure with chelate triazenide and *trans* phosphine ligands (*142a*).

Rhenium(I) triazenide complexes Re(ArNNNAr)$(CO)_2(PPh_3)_2$ prepared by a parallel method have been shown by X-ray diffraction methods (Ar = *p*-tolyl) to possess a similar structure (*87*). The reaction of $ReH(CO)_2(PPh_3)_3$ with *p*-tolyl azide affords Re(HNNN-tol-*p*)$(CO)_2(PPh_3)_2$ (*107*). Reduction of $ReOCl_2(PPh_3)_2$ with excess triphenylphosphine in the presence of lithium triazenides yields paramagnetic rhenium(III) complexes Re(ArNNNAr)$Cl_2(PPh_3)_2$, one of which (Ar = *p*-tol) has been shown to possess a distorted octahedral structure with a chelate triazenide ligand and a trans pair of phosphines (*192*). On heating under reflux in CCl_4 solution this complex decomposes to form the nitrene species $ReCl_3$(N tol-*p*)$(PPh_3)_2$ in good yield (*193a*). A symmetrical trinuclear structure with chelate triazenide ligands has been proposed on the basis of molecular weight and spectroscopic data for the brown product $Re_3Cl_3(CH_2SiMe_3)_3(PhNNNPh)_3$, obtained by treatment of $Re_3Cl_3(CH_2SiMe_3)_6$ with diphenyltriazene (*75*).

4. *Iron, Ruthenium, and Osmium*

High yields of the moisture-sensitive tris(chelates) $Fe(ArNNNAr)_3$ have been obtained by shaking anhydrous iron(III) chloride with silver(I) triazenides in dry ether at room temperature (*18*). Silver triazenides also react with the iron complexes $FeX(C_5H_5)L_2$ [L = PPh_3, $P(OMe)_3$, $P(OPh)_3$, or CO] via unstable binuclear species "$(C_5H_5)LFe(ArNNNAr)AgX$" to give the chelate triazenide complexes $Fe(ArNNNAr)(C_5H_5)L$ (**13**). The complexes have been shown by ^{31}P and ^{13}C NMR to be rigid on the NMR timescale (*183*). The reversible electrochemical oxidations shown in Eq. (22) occur in



(13)

$$Fe(ArNNNAr)(C_5H_5)L \rightleftharpoons [Fe(ArNNNAr)(C_5H_5)L]^+ \qquad (22)$$

the potential range 0.25–0.65 V using an Ag–AgI electrode in CH_2Cl_2 solution. However, attempted chemical oxidation with $NO{\cdot}PF_6$ affords iron(II) nitrosyl derivatives $[Fe(ArNNNAr)(C_5H_5)(NO)(CO)][PF_6]$, which are thought to contain monodentate triazenide ligands (*214*).

Several series of chelate diaryl triazenide complexes of ruthenium have been reported. The hydrides $RuH_2(PPh_3)_4$, $RuH_2(CO)(PPh_3)_2$, and $RuHCl(CO)(PPh_3)_3$ react with free diaryltriazenes to afford the brightly colored, air-stable complexes $Ru(ArNNNAr)_2(PPh_3)_2$, $RuH(ArNNNAr)(CO)(PPh_3)_2$, and $RuCl(ArNNNAr)(CO)(PPh_3)_2$, respectively (*135*, *190*). Lithium triazenides react with $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ to yield $Ru(ArNNNAr)_2(PPh_3)_2$ and $RuH(ArNNNAr)(PPh_3)_3$, respectively (*120*). Finally, free triazenes react with $RuCl_2(PPh_3)_3$ and $RuCl_2(CO)(PPh_3)_3$ in the presence of base (NEt_3) to form $Ru(ArNNNAr)_2(PPh_3)_2$ and $RuH(ArNNNAr)(CO)(PPh_3)_2$, respectively (*54*), and with $RuCl_2(PPh_3)_3$ in the presence of air to form $RuCl_2(ArNNNAr)(PPh_3)_2$ (*41*). A distorted octahedral structure [$\angle N—Ru—N = 57.7(1)°$] with trans phosphine ligands has been reported for $RuH(p\text{-tol-NNN-tol-}p)(CO)(PPh_3)_2$; the symmmetrical nature of the chelate triazenide ligands is confirmed by the N—N bond lengths [1.318(4) and 1.310(4) Å] (*20*).

Nonrigid seven-coordinate osmium trihydrides, $OsH_3(ArNNNAr)(PPh_3)_2$, have been obtained by treatment of $OsH_4(PPh_3)_3$ with diaryltriazenes in refluxing benzene/2-methoxyethanol (*135*, *190*). Similar reactions involving $OsHCl(CO)(PPh_3)_3$ or $OsH_2(CO)(PPh_3)_3$ afford the complexes $OsH(ArNNNAr)(CO)(PPh_3)_2$ (*135*, *190*). A single-pot reaction between Na_2OsCl_6, diaryltriazene, and base (KOH) in refluxing 2-methoxyethanol affords the products *cis*-$Os(ArNNNAr)_2(PPh_3)_2$ (*135*). Osmium(III) triazenides, $OsX_2(PhNNNPh)(PPh_3)_2$ ($X = Cl$ or Br) have been obtained by treatment of the osmium complexes *trans*-$Os(O)_2X_2(PPh_3)_2$ or $OsCl_4(PPh_3)_2$ with Li[PhNNNPh]. The green paramagnetic products exhibit X-band ESR spectra (CH_2Cl_2 solution, $-160°C$, g values ~ 2.7, 2.1, and 1.0) consistent with d^5 low-spin osmium(III) in a low-symmetry environment (*3*). Reactions between osmium carbonyl clusters and various organic azides have yielded complexes in which triazenide ($HN{=}N{-}NH^-$) and monosubstituted triazenide ($RN{=}N{-}NH^-$) anions are stabilized as coordinated ligands. The parent triazenide complex $Os_3(\mu\text{-}H)(\mu\text{-}HNNNH)(CO)_{10}$, obtained from Me_3SiN_3 and $Os_3H_2(CO)_{10}$ after heating under reflux in hexane for 24 hours, has been shown to possess a triazenide-bridged structure (Fig. 9) (*113*). Corresponding reactions using alkyl or aryl azides RN_3 ($R = Bu^n$, Cy, Ph, Bz, or $C\{Ph\}{=}CH_2$) afford mono-substituted triazenide derivatives $Os_3(\mu\text{-}H)(\mu\text{-}HNNNR)(CO)_{10}$, one of which ($R = Ph$) has been shown to possess a similar structure (**14**) (*26*, *43*).

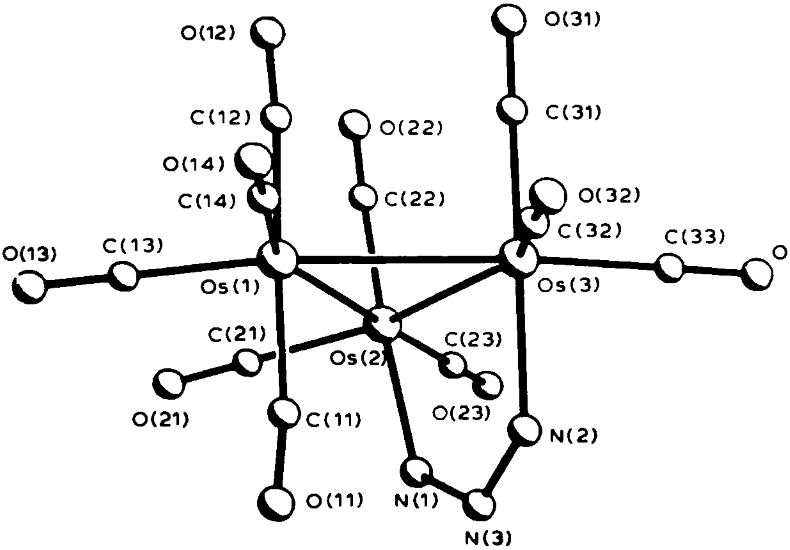
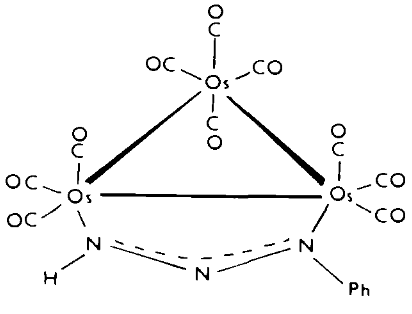


FIG. 9. Molecular structure of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}HNNNH)$.



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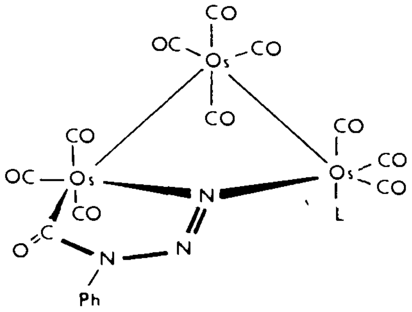


(15)

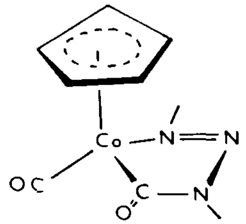
Thermolysis of these products generates the face-capped nitrenes $Os_3(\mu\text{-}H)_2(\mu_3\text{-}NR)(CO)_9$ (*24*). The substituted clusters $Os_3(CO)_{11}L$ react with phenyl azide to give the products $Os_3(CON_3Ph)(CO)_{10}L$, whose structures (**15**, L = py or MeCN) have been established by diffraction methods (*25*).

5. Cobalt, Rhodium, and Iridium

The first cobalt triazenide complex $Co(ArNNNAr)_2$ (Ar = $p\text{-}C_6H_4NO_2$) was obtained by Meldola and Streatfeild in 1887 from an ammoniacal solution of $Co(NO_3)_2$ and $NH_4[ArNNNAr]$ (*146*). A cobalt(III) triazenide $Co(p\text{-tol-NNN-tol-}p)_2(NO_2)(H_2O)$ was reported in 1908 (*108*). X-Ray crystal structure determinations have been published for the monoclinic (*47*, *49*) and trigonal (*127*) forms of $Co(PhNNNPh)_3$. Both confirm the tris(chelate) structure and the strain within the chelate rings ($\angle$N—Co—N = ~ 65°, $\angle$N—N—N = ~105°). The original synthesis of tris(triazenide)cobalt(III) complexes does not appear to have been published (*67*), but a more recent paper (*137*) mentions a route based on the thermal decomposition of the bis(pyridine) adducts $Co(ArNNNAr)_2py_2$. A brief note (*225*) mentions the synthesis of cobalt(II) and cobalt(III) triazenides from the corresponding acetates or nitrates and arylamines in the presence of isoamyl nitrite. Magnetic data and electronic spectra have been reported for the cobalt(III) complexes $Co(ArNNNAr)_3$ (μ_{eff} = ~0.44–0.72 BM) and for the cobalt(II) adducts $Co(ArNNNAr)_2py_2$ (μ_{eff} = 5.08–5.43 BM) (*137*). The compound *mer*-$CoMe_3(PMe_3)_3$ reacts with Me_3SiN_3 to form the azide $Co(N_3)Me_2(PMe_3)_3$; however, with *p*-tolyl azide, a formal "insertion" reaction generates the green air-sensitive triazenide complex $CoMe_2(p\text{-tol-NNNMe})(PMe_3)_2$ (*trans*-PMe_3 isomer) (*40*). Treatment of the complexes $CoI_2(C_5H_5)L$ [L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$] with silver(I) triazenides, followed by anion exchange with $TlPF_6$, affords triazenide chelate salts $[Co(ArNNNAr)(C_5H_5)L][PF_6]$ (*177*). Electrochemical reduction of these salts (-0.2–$+0.1$ V versus an Ag/AgCl electrode in acetone solution) affords the cobalt(II) products $Co(ArNNNAr)(C_5H_5)L$ (*214*). The cobalt(II) derivatives ($L = PPh_3$) have also been obtained by treatment of $CoCl(C_5H_5)(PPh_3)$ with copper(I) or silver(I) triazenides, and can be reoxidized using $AgPF_6$ (*177*).

$$Co(ArNNNAr)(C_5H_5)(PPh_3) + AgPF_6 \longrightarrow [Co(ArNNNAr)(C_5H_5)(PPh_3)][PF_6] + Ag^0 \qquad (23)$$

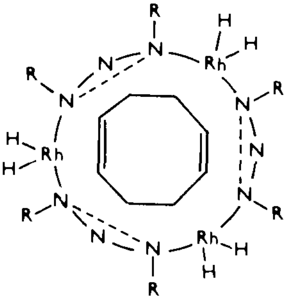
Poorly resolved ESR spectra for the complexes $Co(ArNNNAr)(C_5H_5)L$ are consistent with low-spin d^7 cobalt(II) in a low-symmetry environment ($g_x \neq g_y \neq g_z$, $g_{iso} = \sim 2.1$) (*178*). The reaction between $CoCl_2(PPh_3)_2$ and silver triazenides affords cobalt(II) species $Co(ArNNNAr)_2$, which can be isolated as the previously known (*137*) pyridine adducts $Co(ArNNNAr)_2py_2$ (*178*). Magnetic data and electronic spectra have been analyzed for the complexes $Co(PhNNNPh)_2$ and $Co(PhNNNPh)_2py_2$ (*84*, *149*). The cobalt(III) triazenide $Co(C_3F_7)(PhNNNPh)(C_5H_5)$ has been obtained from $CoI(C_3F_7)(C_5H_5)(CO)$ and Na[PhNNNPh] (*118*). However, reaction of $CoI_2(C_5H_5)(CO)$ with silver(I) triazenides is accompanied by a carbonyl "insertion" step leading to formation of the products $\overline{Co\{RNNN(R)C}(O)\}(C_5H_5)(CO)$ (**16**) (*177*). The first stable metal "phosphazide" complex $Co\{Cy_3P{=}N{-}N{=}NC(O)C_4H_3O\}Br_2$ has been obtained by treatment of $CoBr_2(PCy_3)_2$ with furoyl azide at 0°C (*9*).



(16)

Diaryltriazenes react with the rhodium precursors $RhCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$, $RhH(PPh_3)_4$, and $Rh(NO)(PPh_3)_3$ to afford the 1,3-diaryl triazenide products $RhCl(ArNNNAr)_2(PPh_3)$, $Rh(ArNNNAr)(CO)(PPh_3)_2$, $RhH_2(ArNNNAr)(PPh_3)_2$, and $Rh(ArNNNAr)_2(NO)(PPh_3)$, respectively (*135*, *190*). Treatment of $RhCl(PPh_3)_3$ and $[RhCl(C_8H_{12})]_2$ with Li[ArNNNAr] yields $Rh(ArNNNAr)(PPh_3)_2$ and binuclear $[Rh(ArNNNAr)(C_8H_{12})]_2$, respectively (*120*). Diaryltriazenes in the presence of base (NEt_3) react with $RhCl(C_8H_{12})(PPh_3)$, $RhCl(CO)(PPh_3)_2$, and $[RhCl(CO)_2]_2$ to afford $Rh(ArNNNAr)(C_8H_{12})(PPh_3)$, $Rh(ArNNNAr)(CO)(PPh_3)_2$, and binuclear

$[Rh(ArNNNAr)(CO)_2]_2$, respectively (*54*). The last-named complexes have also been obtained by treatment of $[RhCl(CO)_2]_2$ with Na[ArNNNAr] (*42*) or $Me_3Sn(ArNNNAr)$ (*1*), and by carbonylation (40 psi, 25°C) of the complexes $Rh(ArNNNAr)(C_8H_{12})$ (*120*). Heterobimetallic complexes (see below), formed between $RhCl(CO)(PPh_3)_2$ and Ag[ArNNNAr], break apart to yield rhodium(I) triazenides $Rh(ArNNNAr)(CO)(PPh_3)_2$ (*129*). The complexes $Rh(ArNNNAr)(C_8H_{12})$ form adducts $Rh(ArNNNAr)(C_8H_{12})(NH_3)$ with ammonia (22 psig, 25°C) and react with dihydrogen to afford $\{RhH_2(PhNNNPh)\}_3(C_8H_{12})$, $\{RhH_2(PhNNNPh)\}_2(C_8H_{14})$, and $\{Rh(p\text{-}F\text{-}C_6H_4\text{-}NNN\text{-}C_6H_4\text{-}F\text{-}p)\}_3(C_8H_{12})$ (*120*). Proton NMR data for $\{RhH_2(PhNNNPh)\}_3(C_8H_{12})$, which show all hydride ligands to be equivalent and to couple to all three ^{103}Rh nuclei, have been taken to indicate the novel macrocyclic structure **17** (*120*). The complexes $Rh(ArNNNAr)(PPh_3)_2$ serve as olefin hydrogenation catalysts (THF, 46 psig H_2) for ethylene and hexene (*120*). They also form adducts $Rh(ArNNNAr)(PPh_3)_2(O_2)$, $Rh(ArNNNAr)(PPh_3)_2(CO)$, and $Rh(ArNNNAr)(PPh_3)_2(NH_3)$, and undergo oxidative addition with MeI and H_2 to form $Rh(ArNNNAr)(Me)I(PPh_3)_2$ and $RhH_2(ArNNNAr)(PPh_3)_2$, respectively (*120*). The triazenide bridged rhodium(I) carbonyl dimers $[Rh(ArNNNAr)(CO)_2]_2$ undergo oxidative addition with I_2 to form rhodium(II) species $[RhI(ArNNNAr)(CO)_2]_2$ (**18**) and are substituted by PPh_3 and dienes (cyclooctadiene, norbornadiene) to yield



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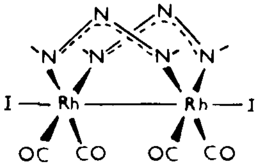

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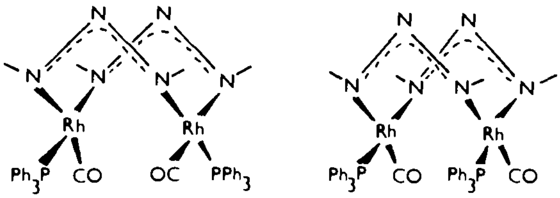
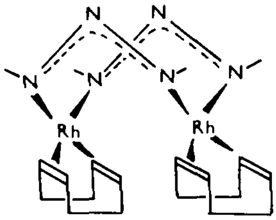


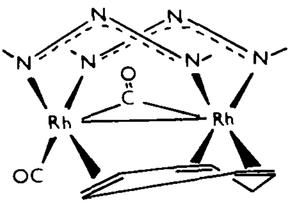
(a) (b)

(19)



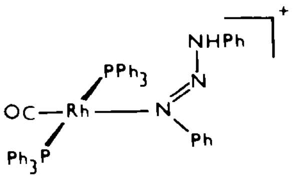
(20)

$[Rh(ArNNNAr)(CO)(PPh_3)]_2$ (**19a/b**) and $[Rh(ArNNNAr)(diene)]_n$ (**20**), respectively (*42*). Ambiguous molecular weight and mass spectroscopic data fail to distinguish between *n* values of 1 and 2 for $[Rh(ArNNNAr)(diene)]_n$, but NMR spectra favor the triazenide-bridged binuclear structure shown. The blue-black products obtained by treatment of $[Rh(ArNNNAr)(CO)_2]_2$ with cycloheptatriene were tentatively assigned structure **21** (*42*). Cycloocta-1,5-diene also affords $Rh_2(ArNNNAr)_2(CO)_2(C_8H_{12})$ (*42*). One-electron electrochemical oxidation of $[Rh(ArNNNAr)(CO)(PPh_3)]_2$ generates the rhodium(I/II) cation $[Rh(ArNNNAr)(CO)(PPh_3)]_2{}^+$ and is accompanied by a decrease in the Rh-Rh distance from 2.96 to 2.67 Å, which is taken to indicate that the electron is lost from an orbital which is anti-bonding with respect to the Rh—Rh bond (*43*). Electron spin resonance spectra for the cation lack fine structure and therefore do not distinguish between delocalized and trapped valence (Rh^I/Rh^{II}) electronic structures. Protonation (HBF_4) of rhodium(I) triazenides $Rh(ArNNNAr)(CO)L_2$



(21)

[L = $PMePh_2$ or $P(C_6H_4\text{-F-}p)_3$] affords the cationic diaryltriazene complexes [Rh(ArNNNHAr)(CO)L_2][BF_4] (*44*), one of which, [Rh(PhNNNHPh)(CO)$(PPh_3)_2$][BF_4], has been shown to possess an N-3-coordinated structure (**22**) (*201*). Treatment of the same complexes (L = PPh_3) with [Ar'N_2][BF_4] leads to formation of the salts [Rh{ArNNN(Ar)C(O)}(N_2Ar')$(PPh_3)_2$][BF_4] (*212*). The binuclear complex [$RhCl_2(C_5Me_5)]_2$ reacts with free triazenes and base or with silver(I) triazenides to afford the chelate triazenide products RhCl(ArNNNAr)(C_5Me_5), which, on treatment with $AgPF_6$ in the presence of donor ligands [L = MeCN or $P(OMe)_3$], form the salts [Rh(ArNNNAr)(C_5Me_5)L][PF_6] (*189*). The azide complex $Rh_2(N_3)_4(C_5Me_5)_2$ forms an adduct $Rh_2(N_3)_4(C_5Me_5)_2$(ArNNNHAr), which has been assigned structure **23** with a labile triazene NH proton, on the basis of infrared and variable-temperature NMR studies (*189*).



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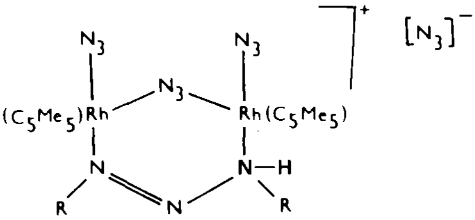
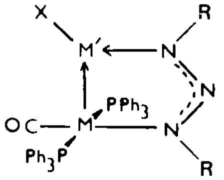


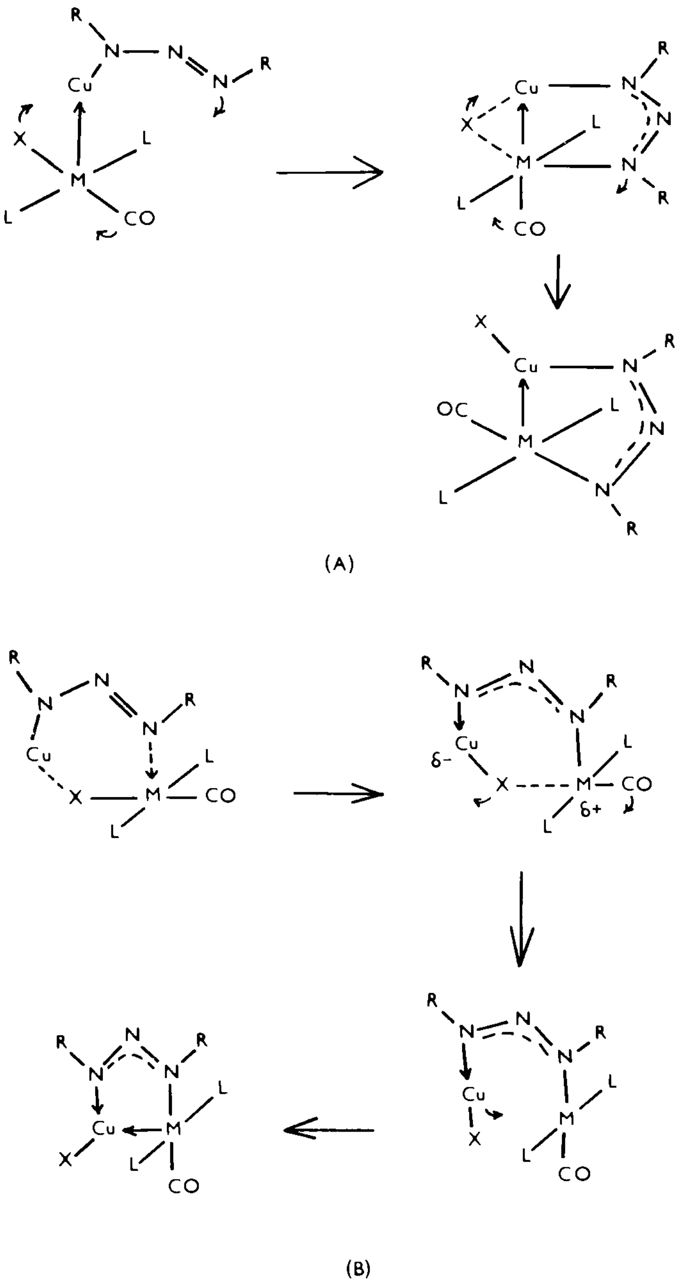
(23)

Iridium precursors *mer*-$IrH_3(PPh_3)_3$ and $IrHCl_2(PPh_3)_3$ react with free diaryltriazenes to form IrH_2(ArNNNAr)$(PPh_3)_2$ and IrHCl(ArNNNAr)$(PPh_3)_2$, respectively. The former products have also been obtained from IrH(CO)$(PPh_3)_3$/ArNNNHAr and by a single-pot synthesis involving Na_2IrCl_6/PPh_3/ArNNNHAr and KOH in boiling 2-methoxyethanol (*135*, *190*). Vaska's complex reacts with lithium (*120*) or silver (*129*) triazenides to yield monodentate triazenide complexes Ir(ArNNNAr)(CO)$(PPh_3)_2$. These in turn add aryldiazonium salts [Ar'N_2][BF_4] to form salts [Ir(ArNNNAr)(N_2Ar')(CO)$(PPh_3)_2$][BF_4] (*212*), and they carbonylate reversibly to yield the carbonyl insertion products Ir{ArNNN(Ar)C(O)}$(CO)_2(PPh_3)$ (*129*). The same precursors undergo protonation by HBF_4 at the metal to yield salts [IrH(ArNNNAr)(CO)$(PPh_3)_2$][BF_4] (contrast the behavior of corresponding rhodium precursors) (*44*). However, triazene complexes [Ir(ArNNNHAr)(CO)$(PPh_3)_2$][BF_4] have been obtained from [Ir(CO)($OCMe_2$)$(PPh_3)_2$][BF_4] by substitution using free triazenes and by solid-state isomerization of the hydrides [IrH(ArNNNAr)(CO)$(PPh_3)_2$][BF_4] (*44*).



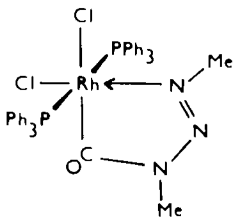
(24)

Vrieze and co-workers have reported the formation of novel triazenide-bridged heterobimetallic complexes (**24**, M = Rh$^{\text{I}}$, Ir$^{\text{I}}$; M′ = Cu$^{\text{I}}$, Ag$^{\text{I}}$; X = Cl, Br, I, or O_2CR; L = P- or As-donor ligand) by addition of copper(I) or silver(I) triazenides to square-planar d^8 rhodium and iridium complexes $MX(CO)L_2$ (*129*, *130*). Thus treatment of $MX(CO)L_2$ with copper(I) triazenides $[Cu(RNNNR')]_n$ ($n = 4$, R = R′ = Me; $n = 2$, R = R′ = *p*-tol or R = Me, R′ = *p*-tol) in refluxing THF affords the air-stable products $L_2(CO)M(\mu\text{-}RNNNR')CuX$, in which the bridging triazenide ligand supports a dative M$^{\text{I}}$ → Cu$^{\text{I}}$ bond (*130*). Directly analogous but somewhat less stable products containing dative (M$^{\text{I}}$ → Ag$^{\text{I}}$) bonds are obtained from silver(I) triazenides Ag(RNNNR′) (R = Me, Et, Bu^t; R′ = Me or *p*-tol) and the precursors $MCl(CO)(PPh_3)_2$ (M = Rh, X = Cl; M = Ir, X = Cl, Br, I, or O_2CCF_3) (*129*, *132*, *219*). These products afford the first examples of compounds containing metal-to-copper(I) (*130*) or -silver(I) (*129*) donor bonds. For both series of reactions, formation of the observed products involves a rather unusual migration of halide or carboxylate ligands from the group VIII metal to the coinage metal. Two possible mechanisms proposed for this process are shown in Scheme 3 (*130*, *219*). The ease of formation and the stability of the products are dependent upon the identity of the metals M and M′, the triazenide bridges, and the auxiliary ligands L (*130*). Generally the rhodium products are less stable than their iridium analogues, possibly because of the greater electron donor capacity of the latter metal (*130*). The five-membered rings formed by the bridging triazenide ligands are thought to possess some delocalized electron density and to play an important role in stabilizing the M → M′ bonds (*130*). Crystal structures reported for $(Ph_3P)_2(CO)M(MeNNNMe)CuCl$ [M = Rh (*124*) or Ir (*125*)] and $(Ph_3P)_2(CO)Ir(MeNNN\text{-}tol\text{-}p)Ag(O_2CPr)$ (*131*) confirm the proposed general structure. Triazene-exchange reactions between $(Ph_3P)_2(CO)Rh(MeNNNMe)AgCl$ and RNNNHR′ (R = Me, *p*-tol; R′ = *p*-tol) have been reported; similar reactions with the corresponding iridium complexes are much slower and lead to decomposition (*129*, *130*). The iridium complexes $(Ph_3P)_2(CO)Ir(RNNNR')AgCl$ (R = Me, *p*-tol; R′ = Me) carbonylate readily to form acyl triazenide products $\overline{\text{Ir}\{\text{R}'\text{NNN(R)C}}\text{(O)}\}(CO)_2(PPh_3)$ (*129*), identical to those obtained from the



SCHEME 3. Mechanisms for the formation of heterobimetallic triazenide complexes. Adapted with permission from *J. Organomet. Chem.* **96**, 289 (1975).

compounds Ir(R'NNNR)(CO)(PPh_3)$_2$ (see above). Vrieze and co-workers have also examined reactions between the complexes MX(CO)(PPh_3)$_2$ and mercury triazenides HgX(RNNNR) or Hg(RNNNR)$_2$, from which they have harvested a rich variety of products (*218*). The rhodium precursor RhCl(CO)(PPh_3)$_2$ reacts with HgCl(MeNNNMe) and HgI(MeNNNMe) to form the acyl derivatives **25** and **26**, respectively. A closely related product (**27**) is obtained from Rh(O_2CCF_3)(CO)(PPh_3)$_2$ and HgI(MeNNNMe).



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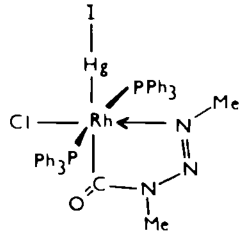

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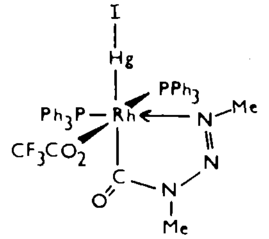

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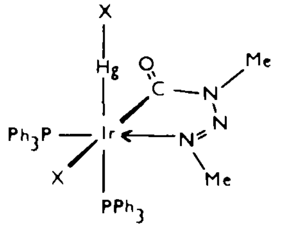

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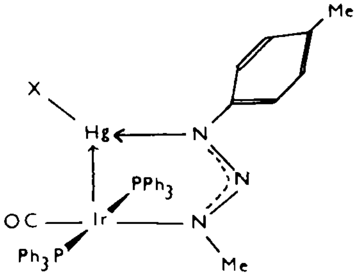
Acyl triazenide complexes **28** are also isolated from reactions between IrX(CO)(PPh_3)$_2$ and HgX(MeNNNMe) (X = Cl, Br, I, or O_2CCF_3), but corresponding reactions involving HgX(*p*-tol-NNNMe) afford triazenide-bridged products **29**. Finally, treatment of the rhodium and iridium complexes MX(CO)(PPh_3)$_2$ with Hg(MeNNNMe)$_2$ generated **30** (*218*). Formation of the M—Hg bonds is relatively easy and less dependent upon the presence of stabilizing bridging ligands (*218*). However, it is not clear why small changes in X, R, and M give rise to such variations in product structure (*218*). The tetranuclear products [(diene)(RNNNR')$_2$MHgCl]$_2$ (M = Rh, Ir; diene = C_8H_{12} or C_7H_8; R = Me, Et, *p*-tol; R' = *p*-tol) have been obtained from the reactions of [MCl(diene)]$_2$ with Hg(RNNNR')$_2$, and of [(diene)MCl·$HgCl_2$]$_2$ with [Ag(RNNNR')]$_n$ (*217*). An X-ray diffraction study reveals the chloride-bridged dimer structure **31**. Variable-temperature ^{1}H- and ^{13}C-NMR establish that the Rh/Hg complexes, but not their Ir/Hg



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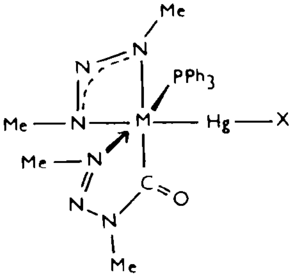

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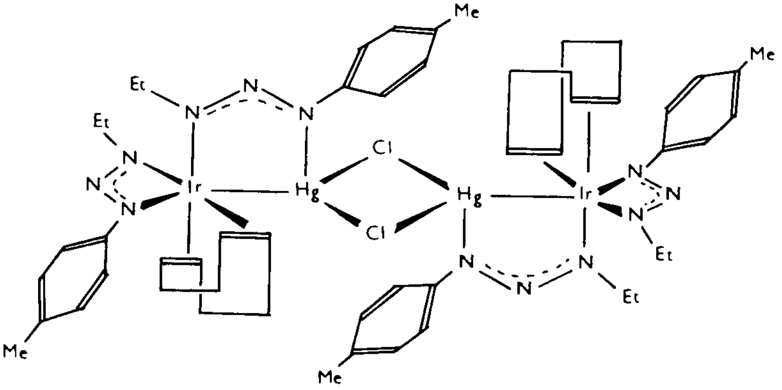


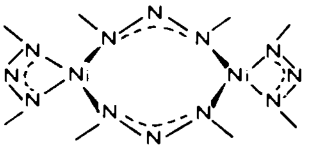
(31)

analogues, are fluxional with chelate and bridging triazenide ligands exchanging via monodentate intermediates (*217*). Attempts to prepare complexes containing Rh/Ir—Tl bonds were frustrated by the instability of thallium(III) triazenides $Tl(RNNNR)_nCl_{3-n}$ ($n = 1$-3) (*220*).

6. *Nickel, Palladium, and Platinum*

An early report by Meldola and Streatfeild (*146*) described an impure sample of $Ni(ArNNNAr)_2$ ($Ar = p\text{-}C_6H_4\text{-}NO_2$). Formation of nickel(II) diaryltriazenide complexes $Ni(ArNNNAr)_2py_2$ by treatment of nickel acetate with triazenes and pyridine followed by base (Na_2CO_3), and the subsequent thermal decomposition of these products to leave the pyridine-free complexes "$Ni(ArNNNAr)_2$," was first reported by Dwyer and Mellor in 1941 (*74*). Prolonged, vigorous treatment of the latter products with pyridine, ethylenediamine (en), and *o*-phenanthroline (*o*-phen) gave the adducts

$Ni(ArNNNAr)_2py_2$, $Ni(ArNNNAr)_2(en)$ (*74*), and $Ni(ArNNNAr)_2$(*o*-phen) (*98*), respectively. Nickel(II) diaryltriazenide complexes have also been obtained from the reactions of arylamines with isoamyl nitrite in the presence of nickel salts (*225*). The paramagnetic character of the pyridine and *o*-phenanthroline adducts ($\mu_{eff} = 3.38$ BM) led to their formulation as polymeric triazenide-bridged derivatives of octahedral nickel(II) (*98*). However, a monomeric structure with chelate triazenide ligands seems more probable. Binuclear chelate/bridging triazenide structures were originally proposed for the complexes $[Ni(ArNNNAr)_2]_n$ (**32**) (*74*). The binuclear character was subsequently confirmed (*98*, *138*), and an alternative triazenide-bridged "lantern" structure (**33**) was advanced (*98*, *99*). An X-ray diffraction study later showed the "lantern" structure to be correct (*46*). Magnetic data and electronic spectra have been recorded and analyzed for $Ni_2(PhNNNPh)_4$ and $Ni(PhNNNPh)_2py_2$ (*84*). Silver triazenides, Ag(RNNNR), react with $NiCl(C_5H_5)(PPh_3)$ in the presence of ligands L [$L = PPh_3$, CO, CNR′] to yield the monodentate triazenide nickel(II) derivatives $Ni(RNNNR)(C_5H_5)L$. When $L = PPh_3$, the complexes are fluxional (Scheme 4). However, when L = CO or CNR, "insertion" occurs to give **34**



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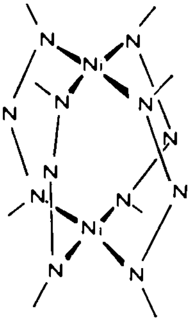

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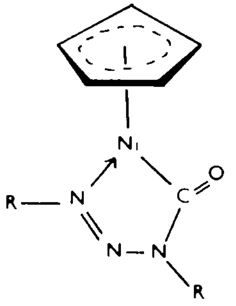

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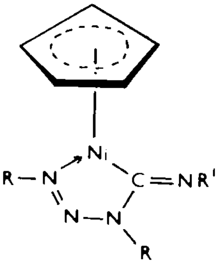

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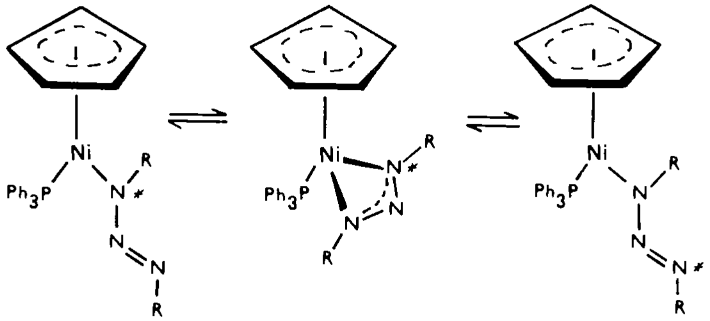
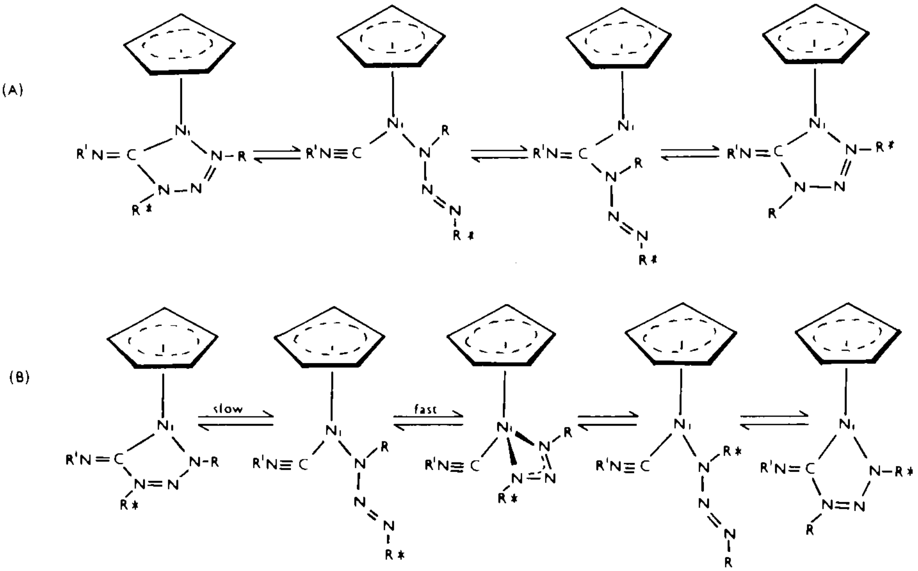


SCHEME 4. Fluxional behavior of the nickel (II) complexes $Ni(RNNNR)(C_5H_5)(PPh_3)$. Reproduced with permission from *Transition Met. Chem* (*Weinheim*) **2**, 240 (1977).

and **35**, respectively (*180*). The isocyanide insertion products are also fluxional (Scheme 5) (*180*).

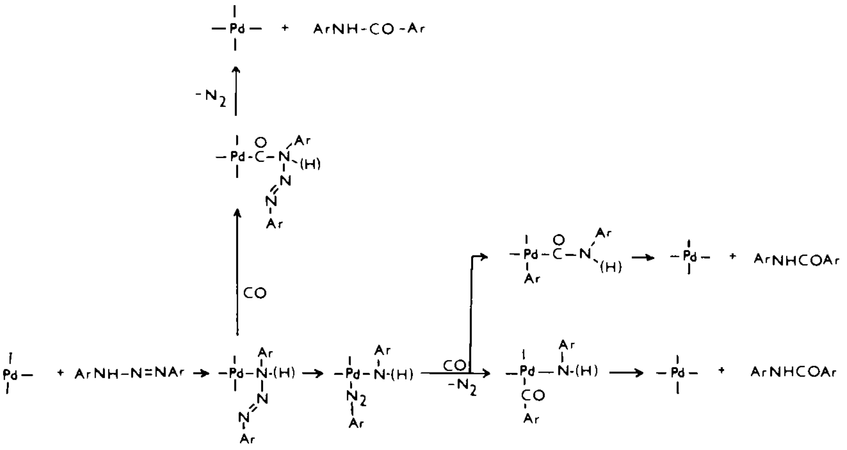
Triazenide complexes of palladium were first described by Dwyer in 1941 (*71*). Addition of Na_2PdCl_4 and sodium acetate to cold aqueous solutions of diaryltriazenes afforded voluminous precipitates of "$Pd(ArNNNAr)_2(ArNNNHAr)$," which readily lost triazene to yield "$Pd(ArNNNAr)_2$" and formed adducts $Pd(ArNNNAr)_2py_2$



SCHEME 5. Fluxional behavior of $Ni\{\overline{RNNN(R)C(NR)}\}(C_5H_5)$. Reproduced with permission from *Transition Met. Chem.* (*Weinheim*) **2**, 240 (1977).

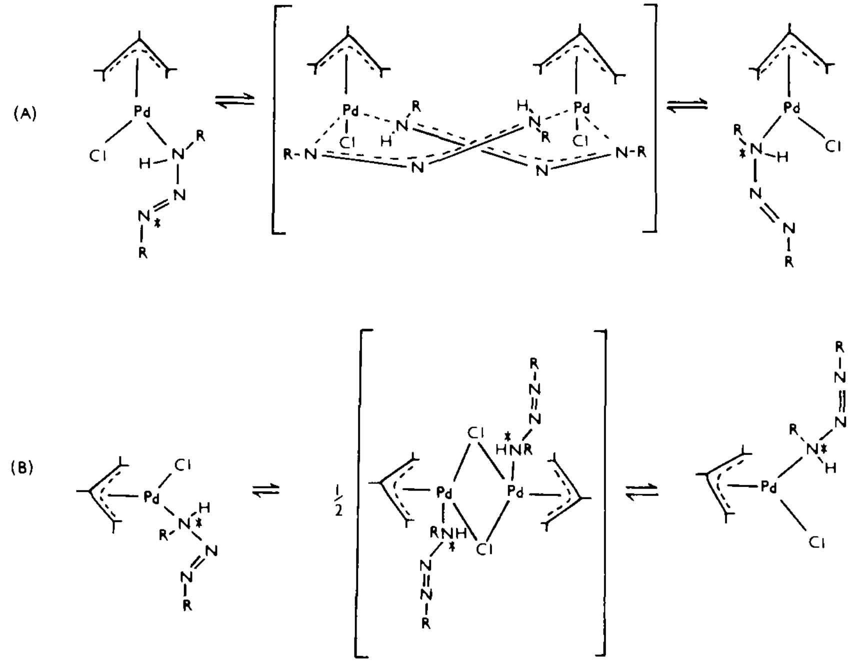
and $Pd(ArNNNAr)_2en$ (*71*). The triazene adducts $Pd(ArNNNAr)_2(ArNNNHAr)$ were claimed as the first examples of octahedral palladium(II) (*71*). However, subsequent attempts to prepare these compounds invariably led to bis-adducts which were formulated as square-planar palladium(II) species (*98*).

The complexes $Pd(ArNNNAr)_2$, which were originally regarded as square-planar bis-chelates (*71*), were subsequently shown by X-ray diffraction methods to possess a binuclear triazenide-bridged "lantern" structure similar to that of the corresponding nickel(II) complexes (*46*). More recently, monodentate triazenide derivatives of square-planar palladium(II) *trans*-$PdCl(ArNNNAr)L_2$ and *trans*- $Pd(ArNNNAr)_2L_2$ ($L =$ phosphine or arsine ligand) have been prepared by treatment of the precursors *trans*-PdX_2L_2 with $ArNNNHAr/NEt_3$ (*54*) or $Li[ArNNNAr]$ (*13*, *209*). The latter products ($L = PPh_3$) have also been obtained from $Pd(PPh_3)_3/ArNNNHAr$ mixtures in warm benzene (*135*, *190*). Confirmation of the square-planar coordination geometry and the monodentate triazenide ligand has been provided by the results of an X-ray diffraction study on *trans*-$PdCl(p\text{-tol-NNN-tol-}p)(PPh_3)_2$ (*13*). The fluxional behavior of these complexes, first reported by Robinson and Uttley in 1972 (*191*), has been confirmed by more recent variable-temperature NMR studies, and a mechanism involving chelate triazenide intermediates (Scheme 1) has been proposed (*54*, *209*). Formation of a palladium triazenide intermediate is thought to be a key step in the $PdCl_2(PPh_3)_2$-catalyzed carbonylation (CO atmosphere) of diaryltriazenes to the corresponding arylamides ArHNC(O)Ar (Scheme 6) (*210*).



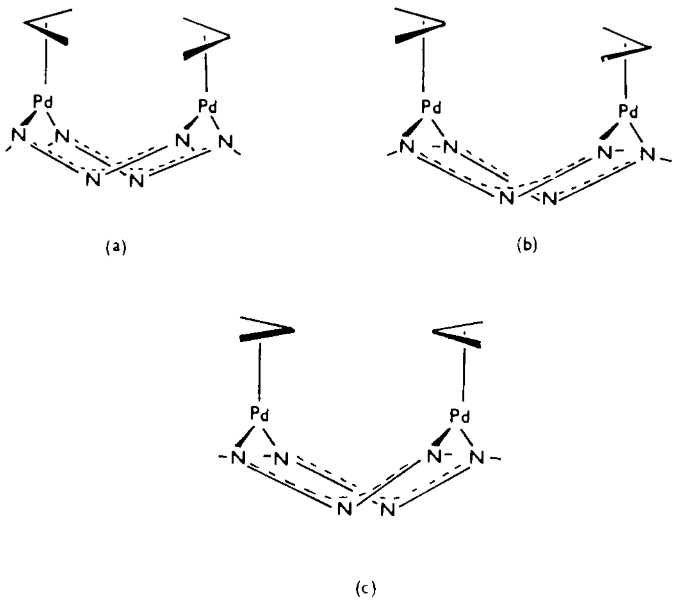
SCHEME 6. Pathway for the $PdCl_2(PPh_3)_2$-catalyzed carbonylation of diaryltriazenes to the corresponding arylamides. Adapted with permission from *Inorg. Chim. Acta* **35**, L367 (1979).

Alkylpalladium chloride dimers are split by aryltriazenes to yield the products $PdCl(\eta^3\text{-}C_3H_5)(ArNNNHAr)$, which participate in two fluxional processes—triazene dissociation and triazene/chloride exchange (Scheme 7A/B). The latter process, which has the lower activation energy, is thought to proceed via a pentacoordinate chloro-bridged intermediate (*14*). Binuclear



SCHEME 7. Fluxional processes for (A) triazene and (B) triazene/chloride exchange in $PdCl(RN{=}N{-}NHR)(allyl)$ complexes. Adapted with permission from *Inorg. Chim. Acta* **34**, 37 (1979).

triazenide-bridged palladium allyls $[Pd(RNNNR)(\eta^3\text{-}C_3H_4R')]_2$ have been obtained by treatment of the corresponding chlorides $[PdCl(\eta^3\text{-}C_3H_4R')]_2$ [R′ = H or Me] with $KOBu^t/ArNNNHAr$ (*102*), $LiBu^n/ArNNNHAr$ (*30*), or Ag(MeNNNMe) (*102, 103*); or by treatment of the acetates $[Pd(O_2CMe)(\eta^3\text{-}C_3H_4R')]_2$ with free triazenes (*111*). X-Ray diffraction studies on $[Pd(p\text{-tol-NNN-tol-}p)(\eta^3\text{-}C_3H_5)]_2$ (*29*) and $[Pd(MeNNNMe)(\eta^3\text{-}C_3H_5)]_2$ (*103*) reveal structures of the form **36a**. In solution, conformer **36a** co-exists with small amounts of **36b** (*30, 111*) and, according to more recent reports, **36c** (*102*). The ^1H NMR spectra of the triazenide-bridged complexes are temperature independent (*30, 111*), and there is no evidence for the operation of nondissociative, low-energy ring flip,



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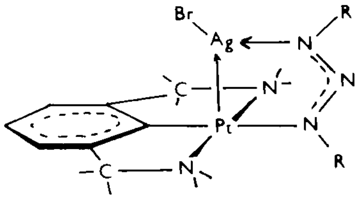
bridge inversion, or bimolecular exchange processes similar to those found for the analogous acetate-bridged complexes (*111*). However the complexes $Pd(ArNNNAr)(C_5H_5)(PPh_3)$, prepared from $PdBr(C_5H_5)(PPh_3)$ and Ag(ArNNNAr), show fluxional behavior (*180*) similar to that observed for the corresponding nickel species.

The early work of Griess on diaryltriazene synthesis included the preparation of complex salts of platinum(II) "$ArNNNHAr{\cdot}HCl{\cdot}PtCl_2$" (*89*). However, most work on platinum triazene complexes is of relatively recent origin. Platinum(II) triazene adducts $PtX_2(ArNNNHMe)_2$ (X = Cl, Br)—incorrectly formulated as $PtX_2(ArNNNMe)_2$ in the original paper—show some evidence of antitumor activity (*116*). The monodentate triazenide derivatives of the four-coordinate platinum(II) compound *cis*-$PtCl(ArNNNAr)L_2$ (L = phosphine, arsine; L_2 = cycloocta-1,5-diene) have been prepared from the corresponding dichlorides and Li[ArNNNAr] (*209*) or $ArNNNHAr/NEt_3$ (*54*), or from *trans*-$PtHCl(PPh_3)_2$ and free triazene (*135*). Treatment of *cis*-$PtCl_2(PPh_3)_2$ with free triazene in the presence of hydrazine affords *trans*-$PtH(ArNNNAr)(PPh_3)_2$ (*208*). X-Ray diffraction studies on PtCl(*p*-tol-NNN-tol-*p*)$(PPh_3)_2$ (*12*, *209*) and PtH(*p*-tol-NNN-tol-*p*)$(PPh_3)_2$ (*109*, *209*) confirm the monodentate nature of the triazenide ligands (Pt—N-3 = 2.908 and 3.008 Å, respectively). Oxidative addition of triazenes ArNNNHAr to $Pt(PPh_3)_3$ affords $Pt(ArNNNAr)_2(PPh_3)_2$ (*135*, *190*). An X-ray diffraction study on *cis*-Pt(PhNNNPh)$_2$(PPh$_3$)$_2$ (Fig. 1) by Brown and Ibers in 1976 provided the first unambiguous structural evidence of monodentate triazenide ligands in a transition metal complex (*21*, *22*). Variable-temperature NMR studies on these platinum(II) triazenide complexes reveal fluxional behavior (*54*, *191*, *208*, *209*) similar to that discussed above for the corresponding palladium(II) complexes. Activation energies are low (≤ 50 kJ/mol) and decrease Pd > Pt. Proton NMR studies on a series of triazenide complexes, *trans*-PtH(ArNNNAr)(PPh$_3$)$_2$, indicate that the triazenide ligand is a good σ donor (*211*). The same complexes react with CO, ArNC, (NC)$_2$CC(CN)$_2$, and PhC≡CPh under mild conditions to yield platinum(0) derivatives by reductive elimination of triazenes (*207*, *208*). The products [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Pt(μ-*p*-tol-NNN-R)AgBr] (R = Me, Et, Pr^i), obtained from {2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}PtBr and [Ag(*p*-tol-NNN-R)]$_n$, have been assigned the Pt → Ag bonded structure **37** on the basis of NMR data. The asymmetry of the triazenide ligands *p*-tol-NNN-R permits two isomeric forms of these complexes, both of which are observed. It has been suggested that the basicity of the platinum atom, enhanced by the N-donor ligands, contributes to the stability of the Pt → Ag dative bond (*215*). An analogous reaction involving HgCl(*p*-tol-NNN-R) produces quantitative yields of [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Pt(*p*-tol-NNN-R)HgBrCl] (**38**). These products can also be prepared from the corresponding carboxylates [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Pt(O$_2$CR)Hg(O$_2$CR)Br and free triazenes, *p*-tol-NNNHR (*216*).



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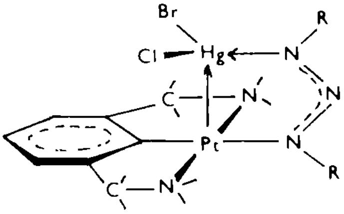

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7. *Copper, Silver, and Gold*

The ability of copper(I) and silver(I) salts to react with triazenes was first noted by Peter Griess in 1866 (*90*), and triazenide complexes of these metals have attracted considerable attention during the intervening years. In marked contrast the first gold triazenide complexes have only recently been reported.

Copper(I) diphenyltriazenide was first properly characterized by Meunier and Rigot (*150*, *152*), who obtained the complex by direct reaction of the free triazene with copper powder. Other copper(I) triazenide complexes, including Cu(PhNNNH) (*64*), Cu(PhNNNMe) (*61*), Cu(PhNNNEt) (*62*), and Cu(MeNNNMe) (*63*), were prepared by Dimroth around the turn of the century. The bis(pyridine) adduct Cu(PhNNNPh)py_2, first described by Dwyer in 1941 (*71*), loses pyridine at 100°C to form Cu(PhNNNPh) as a lemon yellow powder. The latter product was first formulated as a Cu^I—Cu^I-bonded dimer (*150*, *152*), but was subsequently shown to possess a triazenide-bridged structure (Fig. 4) (*19*). In contrast, the corresponding dimethyl triazenide derivative, which was more recently obtained from CuCl and $Al(MeNNNMe)_3$ (*17*), has been found to possess a novel tetranuclear structure (Fig. 5) (*161*). The original suggestion that triazenes existed in cis and trans isomeric forms—"malenoid" and "fumaroid"—which gave rise to different colored copper(I) and silver(I) complexes (*140–142*), was later proved to be incorrect; color differences were attributed to impurities (*69*).

A diaryl triazenide complex of copper(II), $Cu(ArNNNAr)_2$ (Ar = p-C_6H_4-NO_2), was obtained by Meldola and Streatfeild in 1887 from an ammoniacal solution of $CuSO_4 \cdot 5H_2O$ and the free triazene (*146*). Similar complexes were mentioned by Meunier (*150*) and subsequently described in more detail by Mangini and Dejudicibus (*142*). Purer compounds were obtained by addition of cupric acetate to the free triazenes in methanol solution (*71*) and by treatment of cupric nitrate with triazene and base in ethanol (*231*). The adducts $Cu(ArNNNAr)_2py_2$ and $Cu(ArNNNAr)_2(en)$ were also described (*71*). A bis-chelate structure was first proposed for the complexes $Cu(ArNNNAr)_2$ (*71*), but this was subsequently discarded in favor of a binuclear "lantern" structure (*98*, *99*), which was later confirmed by an X-ray diffraction study on the diphenyl triazenide derivative (*45*, *46*). However, molecular weight data for some copper(II) triazenides $Cu(ArNNNAr)_2$ (Ar = p-Cl-C_6H_4, p-Me-C_6H_4) favor a mononuclear $\rightleftharpoons$ dimer equilibrium (*138*) and a combination of molecular weight and magnetic data indicates that copper(II) complexes of bis(trichlorophenyl)triazenes are paramagnetic monomers (*235*, *236*). Infrared and electronic spectra have been discussed for $Cu(p\text{-tol-NNN-tol-}p)_2$ (*237*). Reactions of arylamines with copper(II) acetate in the presence of isoamyl nitrite provide a convenient route to copper(II) triazenide complexes (*225*). Thermal decomposition of copper(II) diaryltriazenides to form the corresponding copper(I) species has been described; side products included N_2, biaryls, and azoaryls (*233*). In the presence of dioxygen, intermediate paramagnetic copper-containing species are formed (*145*). A series of papers by Russian workers record the synthesis and spectroscopic properties of a wide range of copper(II) diaryl triazenide complexes (*79*, *194*, *206*, *235–237*). Magnetic data and electronic spectra have been recorded for $Cu_2(PhNNNPh)_4$ (*84*), and polarographic reduction data have been reported for Cu^I and Cu^{II} diphenyl triazenide complexes (*27*).

Following the initial brief report by Griess (*90*), silver triazenide complexes were next mentioned by Meldola and Streatfeild (*146*), who, in 1887, described the bright red, thermally unstable compound "ArNNNAgAr" (Ar = *p*-C_6H_4-NO_2), obtained from the free triazene and silver nitrate in ammoniacal solution, and who later prepared other silver triazenides by this method (*147*, *148*). This approach was subsequently employed by Dimroth to prepare Ag(MeNNNMe) (*63*), Ag(PhNNNH) (*64*), Ag(PhNNNMe) (*61*), and Ag(PhNNNEt) (*62*), and by Mangini (*140*) and Dwyer (*69–71*) in the 1930s to prepare a range of silver diaryl triazenide complexes. In 1897 Niementowski and Roszkowski (*159*) obtained Ag(PhNNNPh) from anilinium sulfate and silver nitrite; a similar reaction involving $AgNO_2$, $ArNH_2$, and aqueous CO_2 was successfully employed by Meunier (*151*) in 1903. More recently, Vernin and co-workers (*225*) prepared silver(I) triazenides from $AgNO_3$ or AgO_2CMe and arylamines in the presence of isoamyl nitrite. Syntheses of silver(I) diaryltriazenide complexes have also been reported by Mangini (*141*). A mononuclear chelate triazenide structure was originally proposed for the silver(I) salts on the basis of molecular weight data obtained for solutions in pyridine (*71*). However, pyridine adduct formation is likely to occur under these conditions, and it has subsequently been suggested that dimeric or polymeric triazenide-bridged structures are more probable for the nonsolvated complexes (*98*). A series of papers from Russian workers report synthesis of silver(I) triazenide complexes and record vibrational and electronic spectra (*194*, *206*, *236*, *237*). A very extensive range of silver(I) triazenide complexes Ag(RNNNR′), in which R and/or R′ are functionalized organic groups, have been reported (*5*, *11*, *16*, *66*, *88*, *119*, *162*, *184–188*, *200*, *229*).

The first gold triazenide complex $[Au(PhNNNPh)]_4$, prepared from AuI and Na(PhNNNPh) in liquid NH_3 (*6a*), forms yellow, air stable crystals with a tetrameric structure similar to that found for $[Cu(MeNNNMe)]_4$ (Fig. 5).

8. *Zinc, Cadmium, and Mercury*

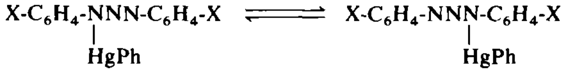
Diethylzinc reacts with dimethyltriazene to afford the moisture-sensitive complex $Zn(MeNNNMe)_2$ (*17*). However, a similar reaction involving diphenyltriazene gave a product which, after recrystallization from dry benzene, was found to be $Zn_4O(PhNNNPh)_6$ and to possess a "basic beryllium acetate" type of structure (*48*).

The first cadmium triazenide complex $Cd(ArNNNAr)_2$ (Ar = *p*-C_6H_4-NO_2) was obtained by Meldola and Streatfeild in 1887 on adding ammoniacal $CdCl_2$ to a hot alcoholic solution of the triazene (*146*). It was described as a steely blue crystalline material which turned red on drying and exploded on heating. The diphenyltriazene analogue, prepared more recently from CdI_2 and Ag(PhNNNPh) in dry ether, forms moisture-sensitive yellow crystals (*18*).

Mercury forms at least three series of complexes with triazenes: the adducts $HgX_2(ArNNNHAr)_2$, and the triazenide derivatives $Hg(ArNNNAr)_2$ and HgX(ArNNNAr) (X = halogen, acetate, aryl, etc.). The adduct $HgCl_2(PhNNNHPh)$ was reported as early as 1897 (*97*). A later report (*139*) that mercury salts HgX_2 form 1/4 adducts $HgX_2(PhNNNPh)_4$ was subsequently refuted (*121*). Attempts to repeat the work gave 1/2 adducts $HgX_2(PhNNNHPh)_2$ (X = Cl, Br) or complexes $Hg(PhNNNPh)_2$ (X = NO_3, $MeCO_2$) (*98*, *121*). The first mercury(II) triazenide complex appears to have been $Hg(PhNNNPh)_2$, obtained by Cuisa and Pestalozza in 1911 from HgO and the free triazene (*55*, *56*). This complex has also been obtained from mercuric acetate and phenylhydrazine (*223*) and from metallic mercury and free triazene in the presence of oxygen (*231*). Numerous papers report the synthesis of mercury(II) triazenides $Hg(ArNNNAr)_2$ (*98*, *140–142*, *205*) or $Hg(O_2CMe)(ArNNNAr)$ (*222*) from mercuric acetate and free triazenes. Two more recent notes describe isolation of $Hg(ArNNNAr)_2$ complexes from the reaction of arylamines with isoamyl nitrite in the presence of mercuric acetate (*225*, *226*). Treatment of mercuric salts HgX_2 (X = Cl, I) with stoichiometric amounts of silver(I) triazenides has been used to generate the complexes HgX(RNNNR′) and $Hg(RNNNR')_2$ (R, R′ = Me or *p*-tol) in solution (*218*).

Several papers report synthesis (*205*) and vibrational, electronic, and proton NMR spectral data (*234*, *235*, *237*) for a range of mercury(II) triazenides $Hg(ArNNNAr)_2$ (Ar = polyhalophenyl). Molecular weight and spectroscopic data indicate that these products are best formulated as monomers with chelate triazenide ligands (*205*, *235*). Core binding energies [C 1*s*, N 1*s*, Hg $4f_{5/2}$, and Hg $4f_{7/2}$] have been measured for a range of mercury(II) triazenides $Hg(p\text{-}X\text{-}C_6H_4\text{-}NNN\text{-}C_6H_4\text{-}X\text{-}p)_2$ (X = H, Me, MeO, or Cl); within limits of error (± 0.2 eV) only a single N 1*s* signal could be detected for each sample. Insensitivity of core binding energies to the nature of the para substituents has been interpreted as evidence of ionic character in the Hg—N bonds (*136*). The high lattice energy, reflected in the low solubility, of the mercury(II) chelates $Hg(ArNNNAr)_2$ apparently causes the species HgX(ArNNNAr) to undergo disproportionation. However, if the aryl groups bear ortho substituents the bis(triazenide) complexes are much more soluble and are thought to contain monodentate triazenide ligands bound to two-coordinate mercury. Using these ortho-substituted diphenyltriazenes it has proved possible to isolate the mixed complexes HgX(ArNNNAr) (X = Cl, Br, I, or CN) by synproportionation of equimolar amounts of HgX_2 and $Hg(ArNNNAr)_2$ (*172*).

Phenylmercuric triazenide complexes PhHg(ArNNNAr), prepared from phenylmercuric hydroxide or acetate and free triazene (*174*) or by synproportionation of $HgPh_2$ and $Hg(ArNNNAr)_2$ (*172, 173, 175*), have attracted considerable attention. An X-ray diffraction study on $PhHg(2\text{-}ClC_6H_4NNNPh)$ has established linear two-coordinate mercury(II) with a monodentate N-1-bonded triazenide ligand (*133*). Multinuclear (^1H, ^{13}C, ^{15}N, ^{19}F, and ^{199}Hg) NMR studies have shown that the 1,3-diaryl triazenide ligands undergo a rapid metallotropic rearrangement, which occurs mainly by an intramolecular mechanism (*126, 157, 174, 175*).



$$\text{X-C}_6\text{H}_4\text{-}\underset{\text{HgPh}}{\text{N}}\text{NN-C}_6\text{H}_4\text{-X} \rightleftharpoons \text{X-C}_6\text{H}_4\text{-NN}\underset{\text{HgPh}}{\text{N}}\text{-C}_6\text{H}_4\text{-X} \qquad (24)$$

Exchange reactions between diaryltriazenes and their phenylmercury derivatives have been examined by proton NMR, and equilibrium constants have been determined (*158*).

III. Tetrazane, Tetrazene, and Tetrazadiene Complexes

Organic derivatives of tetrazane ("buzane") $H_2N{-}NH{-}NH{-}NH_2$ have been known since 1893 (*227*), but to date no transition metal tetrazane complexes have been fully characterized. However, iron tetrazane species have been proposed as intermediates in the iron(II)-catalyzed aerobic oxidation of hydrazines (*104, 230*) and are thought to account for the red coloration observed in some of these reactions (*230*).

The first tetrazene $Et_2N{-}N{=}N{-}NEt_2$ was reported by Fischer (*81*) in 1878 and the first complex, $HgCl_2(Et_2N{-}N{=}N{-}NEt_2)$, was described shortly thereafter (*82*). Despite the ready availability of these ligands, remarkably little further work has been reported and examples of characterized complexes are restricted to metals of group IIB and possibly molybdenum. However, a tungsten complex containing a bridging isotetrazenide (N_4^{4-}) anion, derived from the unknown isotetrazene $(H_2N)_2N{=}N$, has recently been reported (see Section III,E,1).

In contrast, tetrazadienes, $RN{=}N{-}N{=}NR$, which are unknown in the free state, are found in a growing number of transition metal complexes. The ligands can be generated *in situ* from organic azides or diazonium cations and, following the discovery of $Fe(MeNNNNMe)(CO)_3$ by Dekker and Knox in 1967 (*59*), an extensive range of transition metal tetrazadiene complexes has been synthesized. Finally, several papers report theoretical calculations on the stability and structure of N_4 ligands bound to transition metals (*196–198*).

A. SYNTHESIS AND PROPERTIES

Tetrazane complexes may form as unstable intermediates during the transition metal catalyzed oxidation of hydrazines. Tetrazene adducts are obtained from the free ligand and the appropriate metal halide. Tetrazadiene complexes are usually prepared by treatment of suitable transition metal complexes with organic azides (*164*) or diazonium salts (*86*).

$$\mathrm{Co(C_5H_5)(CO)_2 + 2PhN_3 \longrightarrow Co(C_5H_5)(PhNNNNPh) + N_2 + 2CO} \tag{25}$$

$$\mathrm{IrCl(CO)(PPh_3)_2 + 2ArN_2{}^+ + 2\mathit{e} \longrightarrow [Ir(ArNNNNAr)(CO)(PPh_3)_2]^+ + Cl^-} \tag{26}$$

Reactions involving transfer of tetrazadiene ligands between metal centers have also been reported (*170*).

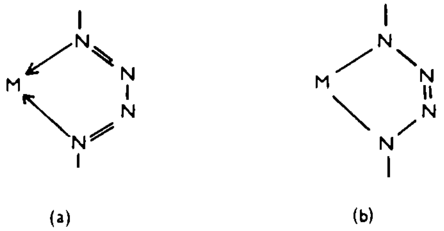
$$\mathrm{Ni(ArNNNNAr)_2 + Ni(Bu^tNC)_4 \longrightarrow 2Ni(ArNNNNAr)(Bu^tNC)_2} \tag{27}$$

Tetrazadiene complexes are noted for their brilliant color and for their stability, which is much greater than that of analogous 1,4-diazabutadiene derivatives.

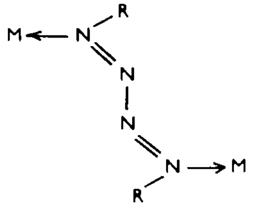
B. STRUCTURAL PROPERTIES

There is no structural information available on tetrazane complexes. Tetrazenes can exist in cis or trans forms, with N-1,N-4-chelation of the cis form originally being advanced as the most probable mode of coordination (*160*). However the only X-ray crystal structure reported to date revealed a trans-tetrazene ligand coordinated through nitrogens N-1 and N-3 (*57*). Tetrazadienes are unknown. However, the parent tetrazabutadiene HN=N—N=NH is isoelectronic with a range of well-known ligands, notably 1,4-diazabutadiene, butadiene, and dinitrogen tetroxide (bound as hyponitrite, $N_2O_4{}^{2-}$). Although there are numerous possible modes of attachment of a four-nitrogen chain to one or more metal centers, only three have assumed importance to date in discussion of metal tetrazadiene structures. There are the η^4-diene structure **39** analogous to that found in

(39)


(a) (b)

(40)


(41)

butadiene iron tricarbonyl, the N-1,N-4-metallocyclic structure **40a/b**, and the N-1,N-4-bridging structure **41**. Theoretical calculations indicate that the η^4-structure (**39**) is likely to be less stable than the N-1,N-4-metallocycle (**40**), and, in keeping with this conclusion, no examples of η^4-tetrazadiene complexes have been reported to date. By virtue of their delocalized π systems, the N-1,N-4-chelated tetrazadienes are "suspect" or "noninnocent" ligands (*86*) like the 1,2-diimines and 1,2-dithiolenes. Consequently, the electronic structures of their complexes may approximate to one of two canonical forms $M^{n+}/RN{=}N{-}N{=}NR$ and $M^{(n+2)+}/RN^-{-}N{=}N{-}N^-R$, represented by **40a** and **40b**, respectively. In some instances the coordination geometry of the metal center fixes the formal oxidation state of the metal and hence the electronic structure of the tetrazadiene ligands. Thus octahedral $Pt(C{\equiv}CPh)_2(ArNNNNAr)(PEt_3)_2$ is clearly a platinum(IV) rather than a platinum(II) complex, and should be formulated as a tetrazenediyl ($ArN^-{-}N{=}N{-}N^-Ar$) derivative (*85*), whereas the pseudo-tetrahedral complexes $Ni(ArNNNNAr)_2$ are best regarded as nickel(0) tetrazadiene derivatives (*167*). In other cases electronic structures are assigned on the basis of theoretical calculations and/or ligand geometry. Structures containing short central N—N bonds are generally regarded as tetrazene-1,4-diyl[3]

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[3] Some authors incorrectly refer to complexes formulated in this manner as tetrazene complexes. In this article we use the term *tetrazadiene* to describe all ligands of stoichiometry RNNNNR, irrespective of the formal bonding mode, and retain the name tetrazene for ligands of the form $R_2NN{=}NNR_2$ (R = H, alkyl, or aryl).

complexes (**40b**), whereas those in which N—N bonds are of essentially equal length are classified as tetrazadiene derivatives (**40a**). Finally, in the case of diaryltetrazadiene complexes, further evidence is provided by the orientation of the aryl groups relative to the plane of the metallocycle. Structures of the type **40a** have aryl groups conjugated to and fully coplanar with the MN_4 metallocycle, whereas those of type **40b** have aryl groups tilted at angles of ~ 45-65 and 130° to the plane (*167*).

Several binuclear structures thought to contain bridging tetrazadiene ligands have been described and others have been postulated as intermediates in tetrazadiene-transfer reactions but none has proved suitable for X-ray diffraction study. Although N-1,N-4 bridging has been cited (*169*, *171*) as the most probable form of linkage, N-1,N-2 or N-1,N-3 bridges cannot be excluded. Some other possible bridging arrangements have also been discussed (*171*). X-Ray diffraction studies reported to date for tetrazadiene complexes are listed in Table II.

C. SPECTROSCOPIC STUDIES

Salient examples of the applications of spectroscopic techniques to the study of tetrazadiene complexes are given below. In most instances, further details are given when the complexes concerned are discussed in Section III,E.

1. Vibrational Spectra

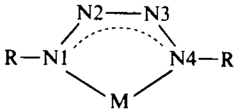
In the absence of spectra for the free ligands relatively little use has been made of infrared and Raman spectroscopy in the study of tetrazadiene complexes. However *prima facie* evidence that the π-acceptor ability of 1,4-dimethyltetrazadiene is comparable to that of a pair of carbonyl ligands is provided by the observation that the degeneracy weighted average $\nu(CO)$ frequency for $Fe(MeNNNNMe)(CO)_3$ is the same (2028.6 cm^{-1}) as that of $Fe(CO)_5$ (*213*). Infrared data [$\nu(NC)$ 2168 and 2146 cm^{-1}] for $Ni(ArNNNNAr)(BuNC)_2$ complexes point to a similar conclusion (*167*).

2. Electronic Spectra

Intense electronic transitions (470–520 and 350–390 nm) exhibited by the complexes $Fe(MeNNNNMe)(CO)_nL_{3-n}$ (L = P-donor, $n = 1$–3) have been attributed to the presence of a low-lying unoccupied metallocycle π^* orbital (*115*, *213*). Electronic spectra have also been reported and analyzed for $[Co(ArNNNNAr)(C_5H_5)]^-$ (*143*), $Co(ArNNNNAr)(C_5H_5)$ (*164*), and $Ni(ArNNNNAr)_2$ (*167*).

TABLE II

SELECTED BOND LENGTHS[a] AND ANGLES[b] FOR TETRAZADIENE COMPLEXES



Molecular formula	R	M—N1/N4	N1—N2/N3—N4	N2—N3	∠α[c]	∠β[c]	Reference
$Fe(RNNNNR)(CO)_3$	Me	1.83	1.32		—	—	*65*
$Co(RNNNNR)(C_5H_5)$	C_6F_5	1.802/1.819	1.360/1.355	1.270	61.45	90.24	*95*
$[Ir(RNNNNR)(CO)(PPh_3)_2][BF_4]$	$4\text{-}FC_6H_4$	1.941/1.971	1.400/1.350	1.270	66	131	*78*
$Ni(RNNNNR)_2$	$3,5\text{-}Me_2C_6H_3$	1.851	1.328	1.309	~0	~0	*167*
$Ni(RNNNNR)(C_5H_5)$	$4\text{-}MeC_6H_4$	1.853/1.843	1.344/1.346	1.278	45.0	44.8	*166*
$Pt(RNNNNR)(C_8H_{12}PEt_3)(PEt_3)$	$4\text{-}NO_2C_6H_4$	2.169/2.159	1.385/1.391	1.263	~0	~0	*165*
$Pt(RNNNNR)(C{\equiv}CPh)_2(PEt_3)_2$	$4\text{-}NO_2C_6H_4$	2.119/2.11	1.41/1.40	1.30	~0	~0	*85*

[a] In angstroms (Å).

[b] In degrees (°).

[c] Dihedral angles between MN_4 plane and the planes of the two aromatic groups R.

3. *Nuclear Magnetic Resonance Spectra*

Routine NMR data have been reported and analyzed for most of the complexes discussed in Section III,E. Multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR studies have proved evidence of fluxional behavior and carbonyl ligand exchange in $Fe(MeNNNNMe)(CO)(PR_3)_2$ (R = Cy, Ph, or OMe) and $Fe(MeNNNNMe)(CO)_3$, respectively (*114*).

4. *Nuclear Quadrupole Resonance Spectra*

Cobalt-59 nuclear quadrupole resonance data have been recorded for $Co(C_6F_5NNNNC_6F_5)(C_5H_5)$ and some related cobalt complexes (*156*).

5. *Electron Spin Resonance Spectra*

ESR data have been used to help characterize the paramagnetic complexes $Ni(ArNNNNAr)(C_5H_5)$ (*166*, *168*) and $[Co(ArNNNNAr)(C_5H_5)]^-$ (*143*).

6. *Photoelectron Spectra*

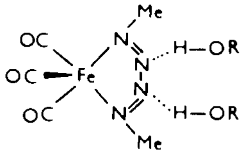
The rich structure observed in the low-energy photoelectron spectrum of $Fe(MeNNNNMe)(CO)_3$ is qualitatively in accord with the fact that there are eight orbitals—arising from the eight *d* electrons of the $Fe(CO)_3$ moiety, and the four π electrons plus two lone pairs of the MeNNNNMe ligand—with ionization potentials in the range 8.1–12.0 eV, and can be assigned on the basis of quantitative Xα calculations (*213*). X-Ray photoelectron spectra have been used to help assign oxidation states in the complexes $Ni(ArNNNNAr)(C_5H_5)$ (*166*) and $Pt(ArNNNNAr)\{\overline{C HC(PEt_3)HCH_2CH_2CH{=}CHCH_2C}H_2\}(PEt_3)$ (*165*).

7. *Mass Spectra*

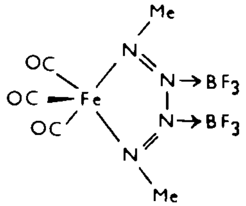
The high thermal stability of tetrazadiene complexes is reflected in their mass spectra, which generally show very intense parent ion peaks. Thus ionization of $Co(MeNNNNMe)(C_5H_5)$ affords a parent ion that fragments with loss of N_2 and Me groups to yield ions which include $[Co(N_2Me)(C_5H_5)]^+$ and $[CoH(C_5H_5)]^+$ (*164*). Field desorption mass spectra have been used to investigate ligand exchange and rearrangement reactions involving tetrazadiene complexes of cobalt, nickel, and platinum (*169*, *171*).

D. CHEMICAL REACTIVITY

In marked contrast to the parent ligands, which are unknown in the free state, tetrazadiene complexes are extremely stable. In particular they are much less susceptible to oxidation, thermal decomposition, or hydrolysis than the analogous complexes of the isoelectronic 1,4-diazadienes. Substitution reactions usually involve the ancillary ligands or occur only when the incoming ligand can attack and destabilize the coordinated tetrazadiene ligand. The latter point is illustrated by the behavior of the complexes $Ni(ArNNNNAr)_2$, which react with Bu^tNC under drastic conditions to afford $Ni(ArNNNNAr)(Bu^tNC)_2$, but resist attacks by CO, PPh_3, or bipyridyl ligands (*167*, *168*). There is good chemical and spectroscopic evidence that tetrazadiene ligands are superior to 1,4-diazadienes and even rival carbon monoxide as π-acceptor ligands (*143*, *213*). The ease with which the complexes $Co(ArNNNNAr)(C_5H_5)$ undergo electrochemical reduction to the corresponding monoanions indicates that tetrazabutadiene ligands are very effective in stabilizing electron-rich organometallics (*143*). The ability of alcohols and, in particular, BF_3 to dramatically increase the rate of CO substitution in $Fe(MeNNNNMe)(CO)_3$ has been attributed to the formation of adducts **42** and **43**, respectively, which make the iron center more susceptible to nucleophilic attack (*33*). Cleavage of tetrazadiene ligands by HCl or HBF_4 to afford ArN_3 and $ArNH_2$ fragments has been reported for several cobalt (*164*), rhodium, iridium, and platinum derivatives (*31*, *134*).



(42)



(43)

$$Pt(ArNNNNAr)(PPh_3)_2 + 2HCl \longrightarrow PtCl_2(PPh_3)_2 + ArN_3 + ArNH_2 \qquad (28)$$

Under the influence of UV radiation the cobalt complex $Co(PhNNNNPh)(C_5H_5)$ undergoes a remarkable transformation to the diimine derivative $Co(HNC_6H_4NPh)(C_5H_5)$ (*93*, *96*). More details of this and some related reactions are given in Section III,E,3. Exchange reactions between tetrazadiene complexes and free aryl azides lead to partial or complete substitution (*169*).

$$Pt(ArNNNNAr)(C_8H_{12}) + Ar'N_3 \longrightarrow Pt(Ar'NNNNAr)(C_8H_{12}) + Pt(Ar'NNNNAr')(C_8H_{12}) \qquad (29)$$

Similar exchange reactions occur rather more slowly between pairs of complexes (*169*).

$$\mathrm{Ni(Ar'NNNNAr')_2 + Ni(ArNNNNAr)_2 \longrightarrow}$$

$$\mathrm{Ni(Ar'NNNNAr')(ArNNNNAr) \xrightarrow{\text{very slow}} Ni(Ar'NNNNAr)(Ar'NNNNAr),\ etc.} \qquad (30)$$

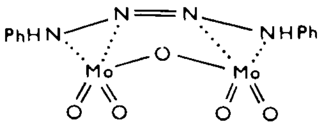
Finally, the ability of tetrazadiene ligands to transfer between metal centers via bridged intermediates has been utilized as a route to new tetrazadiene complexes (*170*, *171*). Further discussion of these exchange and transfer reactions is given in Section III,E,4.

E. GROUP SURVEY

There appears to be no chemistry of tetrazenes or tetrazadienes with metals of the scandium, titanium, and vanadium groups.

1. Chromium, Molybdenum, and Tungsten

The tetrazene-bridged structure **44** has been tentatively proposed for the complex obtained from the reaction of phenylhydrazine with molybdate(VI) anions (*15*). More recently, a novel reaction between the tungsten nitride $W(N)Cl_3$ and the azide $W(N_3)Cl_5$ in the presence of $[Ph_4As]Cl$ has afforded $[Ph_4As]_2[Cl_5W(\mu\text{-}N_4)WCl_5]$, the first example of a complex containing the highly unusual Y-shaped μ-isotetrazenide(4^-) ligand, $N_4{}^{4-}$ (*144*). The X-ray crystal structure (Fig. 10) reveals a bridging planar N_4 moiety linked to the tungsten atoms by very short W—N bonds [1.65(1) and 1.62(1) Å] (*144*).



(44)

No tetrazene or tetrazadiene complexes have been reported to date for members of the manganese, technetium, rhenium triad.

2. Iron, Ruthenium, and Osmium

The first tetrazadiene complex, $Fe(MeNNNNMe)(CO)_3$, which was isolated from the mixture of products obtained on treatment of $Fe_2(CO)_9$ with methyl azide, is a volatile orange solid of remarkable stability (*59*). On

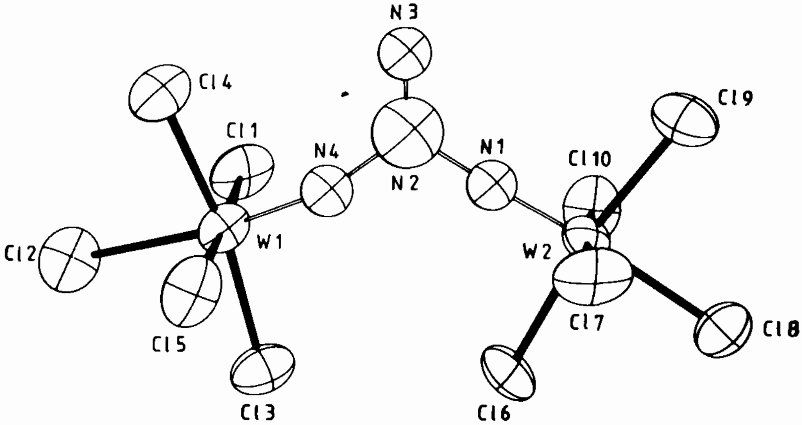


FIG. 10. An ORTEP diagram of the $[Cl_5W(\mu\text{-}N_4)WCl_5]^{2-}$ anion in the crystal of the tetraphenylarsonium salt.

the basis of infrared, NMR, and mass spectroscopic data the original authors proposed a "piano stool" structure analogous to that of butadiene iron tricarbonyl (*59*). However, an X-ray diffraction study quickly established that the MeNNNNMe ligand is bound in chelate fashion (Fig. 11) to generate an essentially planar FeN_4 metallocycle (*65*). Short Fe—N bonds (1.83 ± 0.03 Å) were taken to indicate considerable back donation from iron *d* orbitals to the π^* antibonding orbitals of the tetrazadiene ligand (*65*). CNDO calculations performed on the electronic structures of the two geometries considered above, in which the N_4 moiety is attached to the iron tricarbonyl fragment in σ or π fashion, confirmed that the chelate structure involving

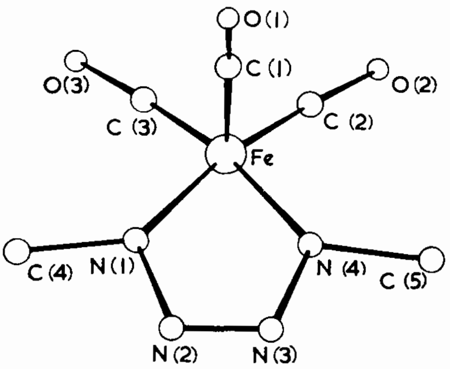
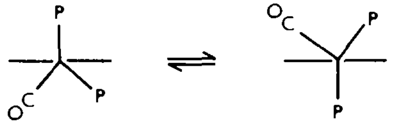


FIG. 11. The molecular configuration of $Fe(MeNNNNMe)(CO)_3$.

bonding between the iron atom and the terminal (N-1 and N-4) nitrogen atoms is the more stable one (*2*). More recently, Hückel molecular orbital and SCC-DV-Xα calculations have been performed on $Fe(RNNNNR)(CO)_3$ (R = Me or Ph) and a series of substituted products $Fe(MeNNNNMe)(CO)_{3-n}L_n$ [n = 1-3, L = PMe_3, PPh_3, or $P(OMe)_3$] (*213*). These are consistent with a structure in which the d^8 $Fe(CO)_3$ fragment possessing two $d\pi$ electrons interacts with the four $p\pi$ electrons of the N_4R_2 ligand to create a six π electron (Hückel aromatic) cyclic system. The SCC-DV-Xα calculations also provide a quantitative explanation of the electronic spectrum, which contains two intense transitions at 470–520 and 349–390 nm attributed to the presence of a low-lying unoccupied metallocycle π^* orbital. In sharp contrast with an earlier CNDO study, which showed a build up of electron density on iron and a decrease of π-electron density on the tetrazadiene ligand, the results of the SCC-DV-Xα calculations point to a flow of electron density from the metal to the tetrazadiene fragment (*213*). Support for this conclusion comes from infrared data (ν_{CO} frequencies) and there is evidence that RNNNNR ligands rival carbon monoxide as π acceptors (*213*). The vapor-phase He 1 photoelectron spectrum of $Fe(MeNNNNMe)(CO)_3$ displays ionizations in the 8- to 11-eV spectral region arising from orbitals containing dominant metal d character in addition to MeNNNNMe lone pair and $p\pi$ character (*213*).

Thermal carbon monoxide substitution in $Fe(MeNNNNMe)(CO)_3$ proceeds readily to form monosubstituted products $Fe(MeNNNNMe)(CO)_2L$ (L = P or As donor, 4-CNpy, or Me_3CNC). With Me_3CNC bi- and trisubstituted species are also obtained (*33*). The substitutions proceed by a second-order mechanism with a rate law which is first order in complex and in entering ligand. Activation parameters, and rates that are strongly dependent upon the nature of the ligand L, particularly its size and basicity, provide further evidence that the substitution reactions proceed by an associative mechanism. A million-fold increase in the rate of substitution, brought about by the addition of excess BF_3, is attributed to the ability of the Lewis acid to withdraw electron density from the iron center and thus facilitate nucleophilic attack by the incoming ligand (*33*). The rate of reaction is also increased by use of polar solvents and, to a greater extent, by use of alcohols which are capable of H bonding to the nitrogens of the tetrazadiene ligands (*33*). In contrast to the corresponding thermal reactions, photosubstitution of CO in $Fe(MeNNNNMe)(CO)_2L$ (L = CO or PPh_3) proceeds via a dissociative mechanism. Products obtained in this manner are of the form $Fe(MeNNNNMe)(CO)_{3-n}L_n$ [n = 1 or 2, L = PPh_3, PMe_3, or $P(OMe)_3$; n = 3, L = $P(OMe)_3$] (*115*). Quantum yields for CO substitution in the parent tricarbonyl increase exponentially as a function of excitation energy from 0.08 (at 578 nm) to 0.53 (at 313 nm) (*115*). Variable-temperature



SCHEME 8. Fluxional process for complexes Fe(MeNNNNMe)(CO)(PR_3)$_2$. Reprinted with permission from *Inorg. Chem.* **21**, 427. Copyright (1982) American Chemical Society.

NMR studies have provided evidence of a fast rocking motion between two distorted square-pyramidal conformations (Scheme 8) for the complexes Fe(MeNNNNMe)(CO)(PR_3)$_2$, and of fast CO and $P(OMe)_3$ exchange in the complexes Fe(MeNNNNMe)$(CO)_3$ and Fe(MeNNNNMe)$\{P(OMe)_3\}_3$, respectively (*114*).

3. *Cobalt, Rhodium, and Iridium*

Shortly after the synthesis of Fe(MeNNNNMe)$(CO)_3$, a similar reaction between organic azides, RN_3, and Co(C_5H_5)$(CO)_2$ was shown to afford air-stable deep green (R = Me) or brown (R = Ph) crystals of stoichiometry Co(RNNNNR)(C_5H_5) (*164*). Physical data and chemical reactivity patterns led to formulation of these complexes as tetrazenediyl (RN^-—N═N—N^-R) derivatives of cobalt(III). Mass spectra showed intense parent ion peaks (*164*). More recently the bis(perfluorophenyl)tetrazadiene derivative Co(C_6F_5NNNNC_6F_5)(C_5H_5) has been prepared and shown by X-ray diffraction methods to possess a metallocyclic structure (Fig. 12) (*94*, *95*), analogous to that found for Fe(MeNNNNMe)$(CO)_3$. The extremely short Co—N distances [1.802(2) and 1.819(2) Å] are consistent with considerable multiple bond character (*94*, *95*). An extended series of complexes Co(RNNNNR)(C_5H_5) (R = Me, Ph, C_6F_5, 2,4-F_2-C_6H_3, and 2,6-Me_2-C_6H_3) has been prepared and subjected to spectroscopic and theoretical study (*95*). Xα-Calculations predict that two $d\pi$ electrons on the Co(C_5H_5) fragment should interact strongly with an empty low-lying π^* orbital of the tetrazadiene ligand to yield metallocyclic π and π^* orbitals. The electronic spectra display three absorptions (600–670, 425–470, and 355–390 nm), which are attributed to one-electron transitions that terminate in the low-lying metallocycle π orbital (*95*). Although the complexes Co(ArNNNNAr)(C_5H_5) (Ar = Ph or C_6F_5) are thermally stable, they react on irradiation with visible or low-energy UV light to form diimine complexes Co($HNC_6X_4NC_6X_5$)(C_5H_5) (X = H or F) (*96*). Evidence of the intramolecular nature of this rearrangement and nitrogen extrusion reaction was provided by cross-over experiments (*96*). The structure of the diimine product (X = F) has been confirmed by X-ray diffraction methods (*92*).

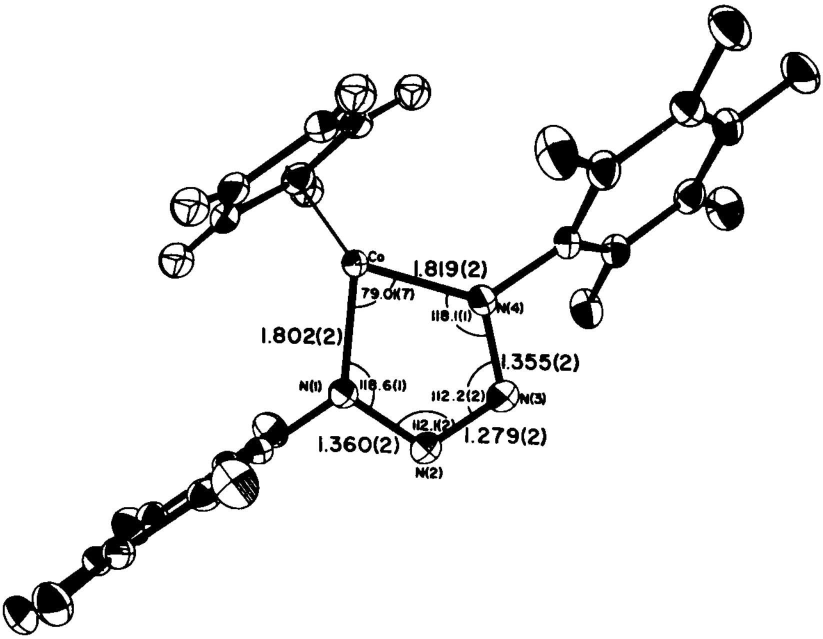
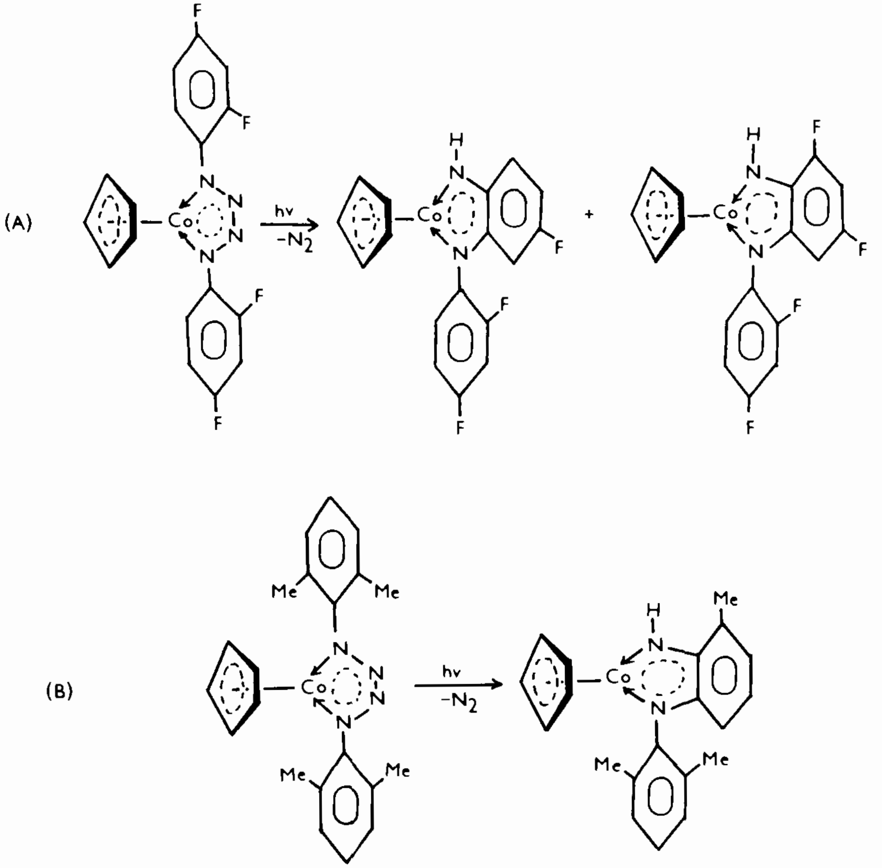


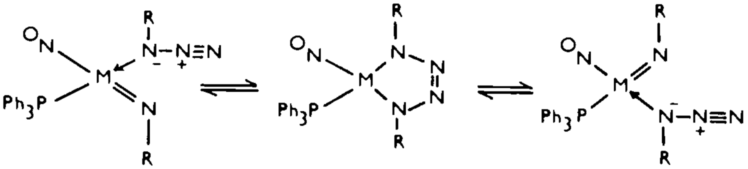
FIG. 12. Molecular structure of $Co(C_6F_5NNNNC_6F_5)(\eta^5\text{-}C_5H_5)$ showing selected bond lengths (in Å) and angles (degrees).

Similar reactions for the complexes $Co(ArNNNNAr)(C_5H_5)$ ($Ar = 2,4\text{-}F_2\text{-}C_6H_3$ or $2,6\text{-}Me_2\text{-}C_6H_3$) yield the products shown in Scheme 9. Aromatic radical substitution processes are proposed to account for the unusual C—C and C—F bond breaking steps (*93*). Aryl azides $Ar'N_3$ react with $Co(ArNNNNAr)(C_5H_5)$ to form $Co(Ar'NNNNAr')(C_5H_5)$; a mechanism involving destabilization and substitution of a complete ArNNNNAr unit has been proposed (*169*). The ^{59}Co nuclear quadrupole resonance spectrum of $Co(PhNNNNPh)(C_5H_5)$ has been recorded (*156*). The paramagnetic d^9 complex anions $[Co(RNNNNR)(C_5H_5)]^-$ ($R = Me$, Ph, C_6F_5, $2,4\text{-}F_2\text{-}C_6H_3$, and $2,6\text{-}Me_2\text{-}C_6H_3$) have been obtained by Na/Hg reduction of the corresponding neutral complexes; one example has been isolated as the brick red dibenzo-18-crown-6-sodium salt $[C_{20}H_{24}O_6Na][Co(PhNNNNPh)(C_5H_5)]$. Reduction potentials (cyclic voltammetry in $CH_3CN/0.1\,M\ Bu^n{}_4NBF_4$) are dependent upon the nature of R and range from -0.71 to -1.53 V. Each anion displays an isotropic ESR spectrum at ambient temperatures ($g = 2.16\text{–}2.26$, $a_{iso} = 50\text{–}58$ G), characteristic of cobalt-centered radicals. These results are consistent with the view that the tetrazadienes are best regarded as neutral π-acid ligands rather than dianions (*143*).



SCHEME 9. Photolytic rearrangements for complexes Co(ArNNNNAr)(C_5H_5). Reprinted with permission from *Inorg. Chem.* **23**, 2968. Copyright (1984) American Chemical Society.

Rhodium and iridium complexes of the form M(RNNNNR)(NO)(PPh_3) (R = *p*-Me-C_6H_4-SO_2-) have been obtained from M(NO)$(PPh_3)_3$ and *p*-toluenesulfonyl azide in benzene. Addition of ligands L (e.g., CO, PPh_3) affords pentacoordinated species M(RNNNNR)(NO)(PPh_3)L. Attempts to form analogous compounds from Co(NO)$(PPh_3)_3$ gave uncharacterizable products. NMR studies provided evidence that was interpreted in terms of an equilibrium (Scheme 10) involving opening of the metallocycle (*134*). However, a later report from the same laboratory concludes that the four-coordinate complexes possess a pseudo-tetrahedral structure and that the splitting of the methyl resonances observed to occur at low temperatures is attributable to a conformational effect (*31*). Cleavage with HCl affords RN_3

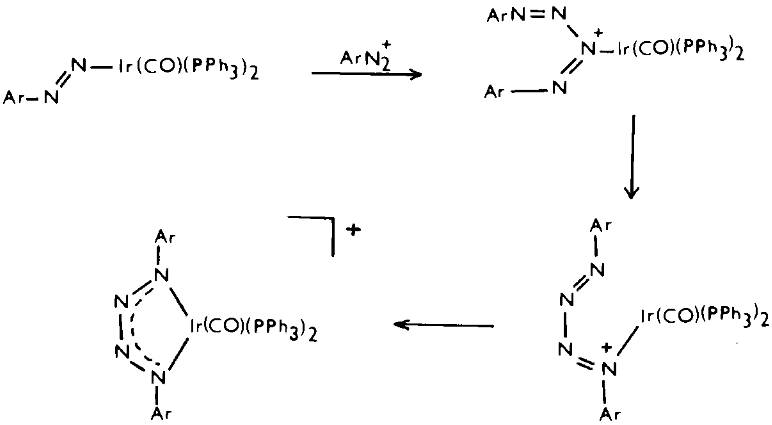


SCHEME 10. Proposed metallocycle cleaving equilibrium for complexes M(RNNNNR)(NO)(PPh$_3$)(M = Rh or Ir). Adapted with permission from *J. Organomet. Chem.* **50**, 287 (1973).

and RNH$_2$ (*31*, *134*). Products from the reactions of diazonium salts [p-R-C$_6$H$_4$N$_2$]BF$_4$ (R = H, F, Cl, Br, MeO, or CF$_3$) with Vaska's compound in benzene/ethanol solution include the bright red, air-stable salts [Ir(p-R-C$_6$H$_4$NNNNC$_6$H$_4$-R-p)(CO)(PPh$_3$)$_2$][BF$_4$] (Scheme 11) (*76*, *77*, *80*, *86*). The same salts have been obtained using IrH(CO)(PPh$_3$)$_3$ in place of IrCl(CO)(PPh$_3$)$_2$ (*80*). The X-ray crystal structure of one example (R = F) has been determined. The iridium coordination geometry approximates to square-pyramidal with an apical PPh$_3$ ligand. The tetrazadiene ligand is coordinated through N-1 and N-4 to generate an IrN$_4$ metallocycle. Bond distances [Ir—N-1, 1.941(13); Ir—N-4, 1.971(10), N-1—N-2, 1.400(16), N-3—N-4, 1.350(16), and N-2—N-3, 1.270(16) Å] are consistent with the tetrazenediyl [RN$^-$—N=N—N$^-$R/Ir(III)] rather than the alternative [RN=N—N=NR/Ir(I)] formulation (*76*, *78*). This conclusion is supported by the results of a semiempirical (CNDO) calculation performed on the simplified model ion [Ir(N$_4$H$_2$)(CO)(PH$_3$)$_2$]$^+$ (*176*).

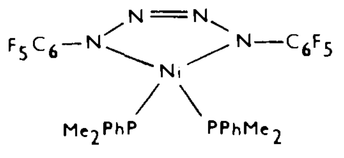
4. *Nickel, Palladium, and Platinum*

The first nickel tetrazadiene complex, Ni(C$_6$F$_5$NNNNC$_6$F$_5$)(C$_8$H$_{12}$), obtained from Ni(C$_8$H$_{12}$)$_2$ and pentafluorophenyl azide, reacts with

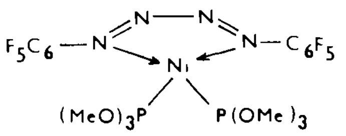


SCHEME 11. Tentative mechanism for the formation of iridium tetrazadiene complexes [Ir(ArNNNNAr)(CO)(PPh$_3$)$_2$]$^+$. Adapted with permission from *Can. J. Chem.* **52**, 3387 (1974).

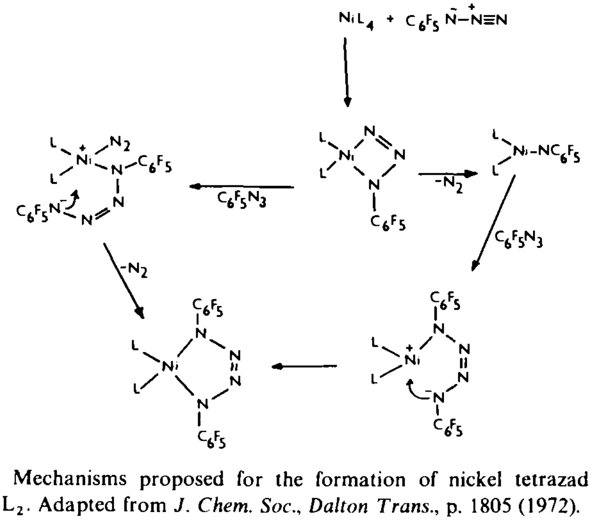
bipyridyl (bipy) and various phosphorus donors [L = PPh_3, PPh_2Me, $PPhMe_2$, or $P(OMe)_3$] to form $Ni(C_6F_5NNNNC_6F_5)(bipy)$ and $Ni(C_6F_5NNNNC_6F_5)L_2$, respectively (*4*). Proton NMR data for complexes containing $PPhMe_2$ and $P(OMe)_3$ have been interpreted in terms of d^8 nickel(II) (**45**) and d^{10} nickel(0) (**46**) structures, respectively. It has been argued that the balance between the two forms is delicately poised and that the structures adopted reflect the good σ-donor and π-acceptor properties of $PPhMe_2$ and $P(OMe)_3$, respectively. Mechanisms for the formulation of these tetrazadiene complexes have been proposed (Scheme 12) (*4*). More recently $Ni(C_8H_{12})_2$ has been shown to react exothermically with aryl azides ArN_3 (Ar = 4-Me-C_6H_4, 4-MeO-C_6H_4, 4-Cl-C_6H_4, or 3,5-Me_2-C_6H_3) to



(45)



(46)



SCHEME 12. Mechanisms proposed for the formation of nickel tetrazadiene complexes $Ni(RNNNNR)L_2$. Adapted from *J. Chem. Soc., Dalton Trans.*, p. 1805 (1972).

form very stable dark purple diamagnetic bis(diaryltetrazadiene) complexes $Ni(ArNNNNAr)_2$ (*167*, *168*). An X-ray diffraction study on one of these products (Ar = 3,5-Me_2-C_6H_3) reveals two mutually perpendicular NiN_4 metallocycles which impart pseudo-tetrahedral geometry to the nickel center (Fig. 13). On the basis of the nickel–nitrogen distances [1.851(2) Å] and the nearly equal nitrogen–nitrogen bond lengths (mean value 1.322 Å) the

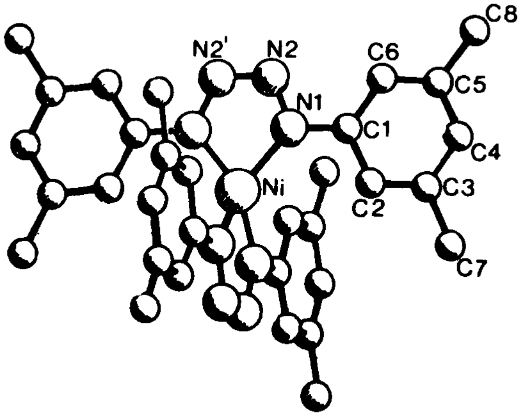


FIG. 13. Molecular structure of Ni(3,5-$Me_2C_6H_3NNNNC_6H_3Me_2$-3,5)$_2$.

complexes are formulated as d^{10} nickel(0) species (*167*, *168*). The reaction of nickelocene with *p*-tolyl azide in boiling toluene affords a 10% yield of a black paramagnetic species Ni(*p*-tol-NNNN-tol-*p*)(C_5H_5) together with a small amount of Ni(*p*-tol-NNNN-tol-*p*)$_2$ (*167*, *168*). ESR spectra for the former product were originally interpreted in terms of a monomeric d^9 nickel(I) complex with an N-1,N-4-chelate tetrazadiene ligand (*168*). The proposed geometry of the complex has been confirmed by X-ray diffraction (*166*). However, the bond lengths for the tetrazadiene ligand [a short central N—N bond [1.278(2) Å] flanked by two longer N—N bonds [1.345(2) Å average] are more in keeping with a d^8 nickel(II)/ArNNNNAr$^-$ or d^7 nickel(III)/ArNNNNAr^{2-} formulation (Fig. 14). Further consideration of ESR and X-ray photoelectron spectroscopy (XPS) data led to the

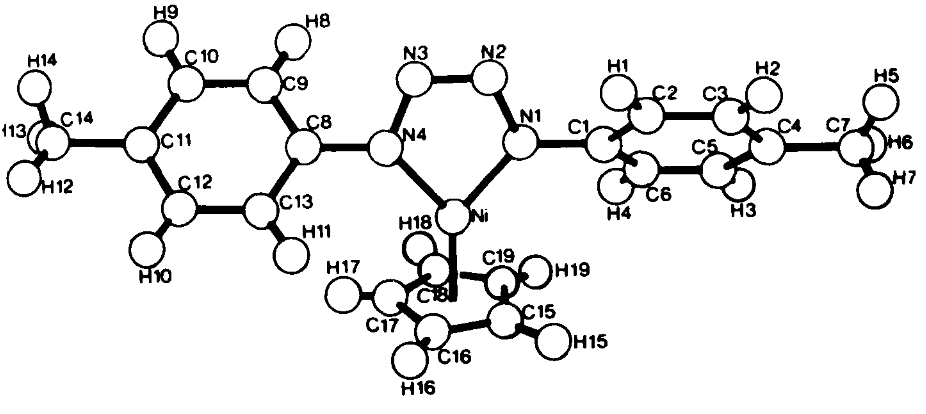
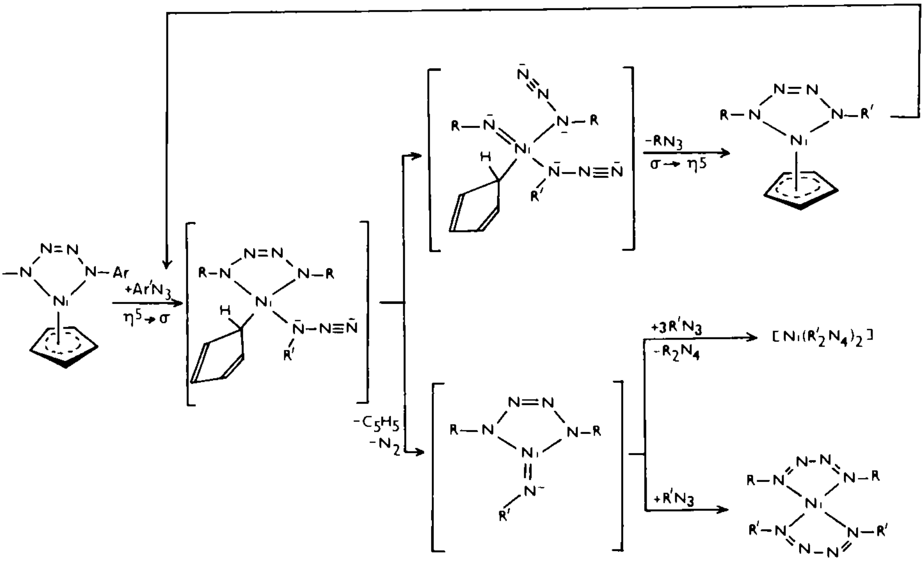


FIG. 14. PLUTO drawing of the molecular structure of Ni(*p*-tol-NNNN-tol-*p*)(η^5-C_5H_5).

conclusion that the complex should be regarded as a d^7 nickel(III) species (*166*). The complex Ni(*p*-tol-NNNN-tol-*p*)(C_5H_5) reacts with *p*-tolyl azide and *t*-butylisocyanide to form Ni(*p*-tol-NNNN-tol-*p*)$_2$ and Ni(*p*-tol-NNNN-tol-*p*)(CNBu^t)$_2$, respectively (*166–168*). The latter product can also be obtained from a 1:1 mixture of Ni(*p*-tol-NNNN-tol-*p*)$_2$ and Ni(CNBu^t)$_4$ in the presence of excess CNBu^t or by treatment of Ni(*p*-tol-NNNN-tol-*p*)$_2$ with excess CNBu^t (*167*). It has been concluded from this work that 1,4-disubstituted tetrazadienes are better π-acceptor ligands than 1,4-disubstituted-1,4-diazadienes or 2,2′-dipyridyl (*166*). A novel route for the synthesis of metal tetrazadiene complexes has recently been reported; direct transfer of ArNNNNAr ligands from Ni(ArNNNNAr)$_2$ to Ni^0 and Pt^0 but not Pd^0 centers in the presence of CNBu^t affords the complexes M(ArNNNNAr)(CNBu^t)$_2$ (*170*, *171*). These ligand-transfer reactions, which require CNBu^t as the co-ligand, are thought to involve binuclear tetrazadiene-bridged species Ni(ArNNNNAr)$_2$ML$_2$, for which tentative structures have been proposed (*171*). Using co-ligands other than CNBu^t it has proved possible to isolate bimetallic Ni/Pd and Ni/Pt complexes analogous to the proposed intermediates (see below). Reactions between pairs of complexes Ni(ArNNNNAr)$_2$ and Ni(Ar′NNNNAr′)$_2$ initially afford mixed products Ni(ArNNNNAr)(Ar′NNNNAr′); after 3–6 days detectable amounts of species such as Ni(ArNNNNAr)(Ar′NNNNAr) are also formed (*169*). Similar results are obtained when mixtures of Ni(ArNNNNAr)$_2$ and Ni(Ar′NNNNAr′)(C_5H_5) are allowed to react. Reactions between nickel complexes Ni(ArNNNNAr)$_2$ or Ni(ArNNNNAr)(C_5H_5) and aryl azides Ar′N$_3$ are more rapid and fall into two categories: (1) those in which only complete tetrazadiene ligands are substituted, and (2) those involving formation of mixed ligands Ar′NNNNNAr. Mechanisms proposed for these reactions are shown in Scheme 13 (*169*).

No simple palladium tetrazadiene complexes have been isolated to date; reactions between Pd(PPh$_3$)$_4$ and organic azides afford polymeric palladium phosphine complexes (*232*). The apparent instability of palladium tetrazadiene complexes has been tentatively attributed to the relatively low basicity of palladium, which does not permit sufficient π back donation to the tetrazadiene ligand (*32*). However, the bimetallic species Ni(*p*-tol-NNNN-tol-*p*)$_2$PdL$_2$ (L = Bu^{t}NC or PEt$_3$) have been obtained from reactions between Pd(norbornene)$_3$ and Ni(*p*-tol-NNNN-tol-*p*)$_2$ in the presence of Bu^{t}NC or PEt$_3$ at 0°C (*170*, *171*).

The first platinum tetrazadiene complexes Pt(RNNNNR)(PPh$_3$)$_2$ (R = PhSO$_2$ or *p*-tolSO$_2$) were prepared by addition of the corresponding azides to Pt(PPh$_3$)$_n$ (n = 4 or, preferably, 3) or Pt(C_2H_4)(PPh$_3$)$_2$, but were originally formulated as bis(aryldiazo) derivatives Pt(N$_2$R)$_2$(PPh$_3$)$_2$ (*7*). The tetrazadiene structure was later proposed by the same authors (*31*). The



SCHEME 13. Proposed mechanisms for ligand scrambling processes in complexes Ni(ArNNNNAr)$_2$. Adapted with permission from *J. Chem. Soc., Dalton Trans.*, p. 1541 (1982).

complexes carbonylate to form Pt(RNNNNR)(CO)(PPh$_3$) and are attacked by HBF$_4$ to liberate azide and amide species, but resist methyl iodide (*31*). Treatment of Pt(CO)$_2$(PPh$_3$)$_2$ or Pt(CO)(PPh$_3$)$_3$ with *p*-toluenesulfonyl azide in dry benzene affords a product Pt(R$_2$N$_4$CO)(PPh$_3$)$_2$ of unknown structure (*8*). Aryl azides ArN$_3$ (Ar = *p*-X-C$_6$H$_4$, X = Cl, NO$_2$, or Me) react with Pt(C$_8$H$_{12}$)$_2$ to yield the products Pt(ArNNNNAr)(C$_8$H$_{12}$) (*168*, *170*), which in turn react with Bu^{t}NC to form Pt(ArNNNNAr)(Bu^{t}NC)$_2$. The latter products can also be obtained from Pt$_3$(CNBu^t)$_6$ and the appropriate azide (*165*, *170*) or by a ligand-transfer process involving Ni(ArNNNNAr)$_2$ and Pt(C$_8$H$_{12}$)$_2$ in the presence of Bu^{t}NC at 60°C (*170*). Under milder conditions the ligand-transfer reactions afford bimetallic intermediates Ni(ArNNNNAr)$_2$Pt(Bu^{t}NC)$_2$ (*170*). Treatment of the complexes Pt(ArNNNNAr)(C$_8$H$_{12}$) with aryl azides Ar'N$_3$ leads to formation of products Pt(ArNNNNAr')(C$_8$H$_{12}$) and Pt(Ar'NNNNAr')(C$_8$H$_{12}$) containing partially and completely substituted tetrazadiene ligands, respectively (*169*). Infrared, NMR, and XPS spectroscopic data indicate that the complexes Pt(ArNNNNAr)L$_2$ (L = Bu^{t}NC, L$_2$ = C$_8$H$_{12}$) are best formulated as derivatives of platinum(II) (*165*). Triethylphosphine reacts with the complexes Pt(ArNNNNAr)(C$_8$H$_{12}$) to afford simple substitution products Pt(ArNNNNAr)(PEt$_3$)$_2$ (Ar = *p*-Me-C$_6$H$_4$, *p*-Cl-C$_6$H$_4$) or to attack the cycloocta-1,5-diene ring (Ar = *p*-O$_2$N-C$_6$H$_4$). The product

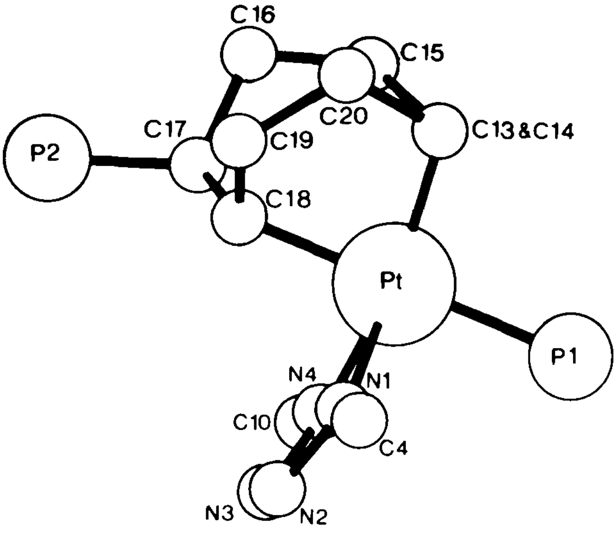


FIG. 15. View of the environment of the platinum atom in $Pt\{\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2}\}(p\text{-}O_2NC_6H_4NNNNC_6H_4NO_2\text{-}p)(PEt_3)$.

of the latter reaction is an intensely blue complex $Pt(ArNNNNAr)\{\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2}\}(PEt_3)$, which has been found by X-ray diffraction methods to possess the structure shown in Fig. 15 (*165*). Reaction of *trans*-$Pt(C{\equiv}CPh)_2(PEt_3)_2$ with ArN_3 ($Ar = p\text{-}O_2N\text{-}C_6H_4$) generates the complex $Pt(ArNNNNAr)(C{\equiv}CPh)_2(PEt_3)_2$, which, on the basis of bond length data, has been formulated as an octahedral platinum(IV) tetrazene-1,4-diyl derivative (*85*).

To date no tetrazene or tetrazadiene complexes of the coinage metals—copper, silver, and gold—appear to have been reported.

5. *Zinc, Cadmium, and Mercury*

No examples of tetrazadiene complexes are known for members of this triad. However, all three elements form complexes with tetrazene ligands $R_2N{-}N{=}N{-}NR_2$.

Colorless tetramethyl-2-tetrazene complexes of zinc, $ZnR_2(Me_2N{-}N{=}N{-}NMe_2)$, have been prepared from the corresponding organozinc compounds ZnR_2 ($R = Bu^t$, Ph, or C_6F_5) and the free ligand in hydrocarbon solvents. Whereas these products are reasonably stable, similar adducts with $ZnBr_2$ and, in particular, $ZnCl_2$ decompose explosively (*160*). Structures involving N-1,N-4-chelated tetrazene ligands were originally proposed (*160*), but an X-ray diffraction study ($R = C_6F_5$) later revealed that the coordinated tetrazene exists in the trans isomeric form and is bound to

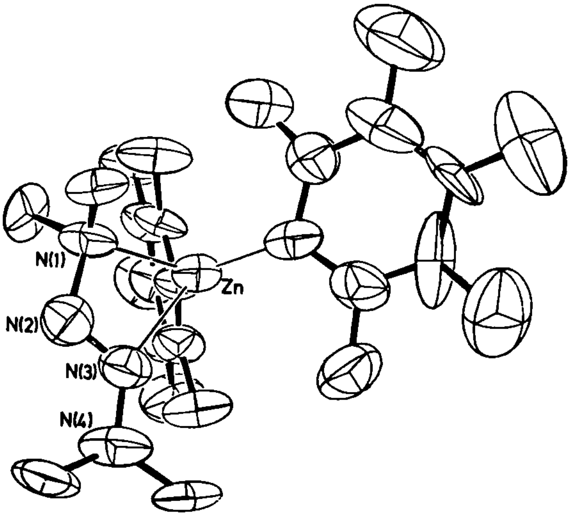


FIG. 16. ORTEP view of the $Zn(C_6F_5)_2(Me_2NN{=}NNMe_2)$ molecule.

the zinc through N-1 and N-3 (Fig. 16) (*57*). This result is in keeping with the report that the parent tetrazene $H_2N{-}N{=}N{-}NH_2$ also has a trans structure (*224*). Variable-temperature ^1H NMR spectra (178–298 K) show a single methyl resonance consistent with fluxional behavior in solution (*57*). Decomposition of $ZnCl_2(Me_2N{-}N{=}N{-}NMe_2)$ in THF affords Me_2N radicals, which can be trapped *in situ* by styrene to form $PhCH(NMe_2)CH_2(NMe_2)$ (*153–155*).

Cadmium complexes $CdX_2(Me_2N{-}N{=}N{-}NMe_2)$ (X = Cl, Br), obtained by addition of the free ligand to alcoholic solutions of cadmium halides, are considerably more stable than their zinc analogues (*23*). Although originally formulated as N-1,N-4 chelates (*23*), it now seems probable that they adopt the N-1,N-3- chelate structures analogous to that established for the related zinc complex (*57*).

The mercury(II) adduct $HgCl_2(Et_2N{-}N{=}N{-}NEt_2)$, first reported by Fischer over 100 years ago (*82*), and the more recently described examples $HgX_2(R_2N{-}N{=}N{-}NR_2)$ (X = Cl, Br; R = C_{1-4} alkyl) (*23, 203*), may well have similar N-1,N-3-chelate structures.

IV. Pentazadiene Complexes

The study of catenated nitrogen ligands has been extended to N_5 systems by the synthesis of transition metal complexes containing coordinated 1,5-diarylpentaza-1,4-diene-3-ide anions (*6*). Although substituted pentaza-1,4-

dienes have been known since 1894 (*228*) and are stable at room temperature, this exciting discovery affords the first examples of their participation in complex formation. Addition of metal amine complexes to solutions of 1,5-di-*p*-tolylpentaza-1,4-diene-3-ide anions in aqueous ammonia yields complexes of the transition metal ions $\mathrm{Cu^{I}}$, $\mathrm{Ag^{I}}$, $\mathrm{Mn^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{Cd^{II}}$, and $\mathrm{Co^{III}}$, as well as a thallium(I) derivative (*6*). The dimeric nickel product $\{\mathrm{Ni}(p\text{-tol-NNNNN-tol-}p)_2\}_2$ was isolated as a paramagnetic ($\mu = 3.1$ BM per Ni atom) brown crystalline powder which decomposes at 120°C. An X-ray diffraction study on monoclinic crystals of a 1:1 THF adduct grown from THF/*n*-hexane solution reveals the structure shown in Fig. 17. Four $\mathrm{N_5}$ zig-zag chains, whose longitudinal axes run parallel, each coordinate to both nickel atoms. Each octahedrally coordinated nickel atom is bound to the N-1 and N-3 atoms of two $\mathrm{N_5}$ chains (Ni—N = 2.13 Å) and to the N-5 atoms of the other two (Ni—N = 2.07 Å).

The initial product of the copper reaction is a brown precipitate of stoichiometry $\mathrm{Cu}(p\text{-tol-NNNNN-tol-}p)_2$, which, on heating, is reduced to deep red, air-stable $\{\mathrm{Cu}(p\text{-tol-NNNNN-tol-}p)\}_3$. The latter product, which is weakly paramagnetic [μ ranges from 0.33 (113 K) to 1.52 BM (303 K)] and decomposes explosively at 160°C, has been found by X-ray diffraction methods to possess the trinuclear structure shown in Fig. 18. Three $\mathrm{N_5}$ zig-zag chains coordinate three linearly arranged copper(I) ions through N-1, N-3, and N-5 atoms, such that each copper is in a trigonal-planar coordination environment. Mean copper–nitrogen distances are 2.036 Å for the outer copper atoms and 1.945 Å for the central copper atom. The copper–copper distances of 2.348 and 2.358 Å are the shortest yet recorded for copper(I) complexes (*6*).

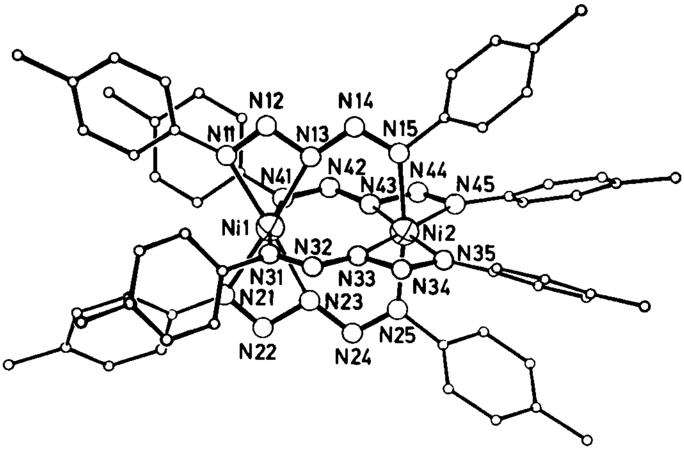


FIG. 17. Molecular structure of $\mathrm{Ni_2}(p\text{-tol-NNNNN-tol-}p)_4$.

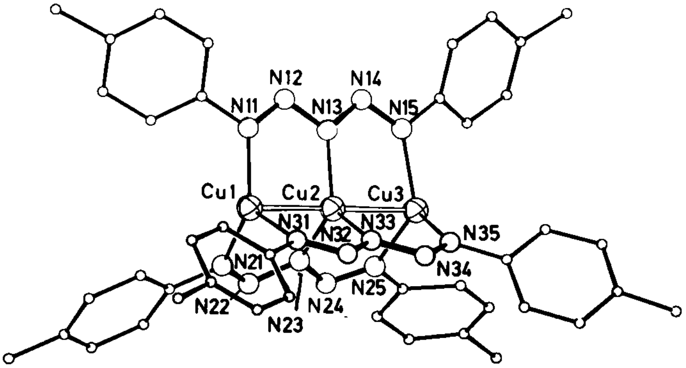


FIG. 18. Molecular structure of $Cu_3(p\text{-tol-NNNNN-tol-}p)_3$.

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