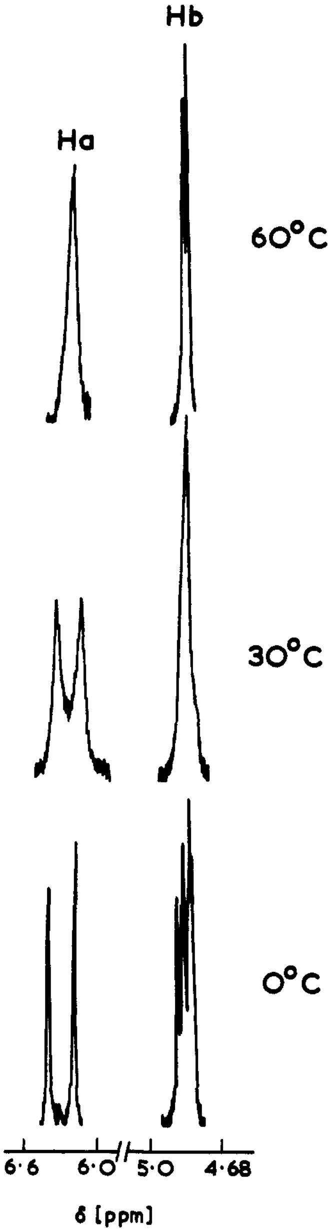

Figure 1. Temperature-dependent nmr of **2b** $\rightleftharpoons$ **3b** in CCl_4.

2b $\rightleftharpoons$ **3b** was found to be solvent dependent, **2b** being favored by 40 cal/mol in CCl_4, while the boat conformer **3b** was stabilized by 600 cal/mol in more polar solvents such as $(CD_3)_2CO$ and $CDCl_3$.

A complete nmr line-shape analysis[8] of the olefinic resonance of the mobile system **2b** $\rightleftharpoons$ **3b** in CCl_4 and in $(CD_3)_2CO$ over the temperature range of full resolution to coalescence (-5 to $+60°$) revealed an energy of activation $\Delta G^{\ddagger} = 16.0$ and 16.4 kcal/mol ($\pm 2\%$), corresponding to $\Delta H^{\ddagger} = 16.7$ kcal/mol and $\Delta S^{\ddagger} = 1.5$ eu ($\pm 50\%$), respectively. The Arrhenius parameters in CCl_4 were $E_a = 17.3$ kcal/mol and $\log A = 13.7$.

Reduction of **2b** + **3b** with hydrogen over Adams' catalyst gave 16-oxatricyclo[11.2.1.1^{2,12}]heptadecan-17-one (**4b**): mp 95°; nmr *inter alia* b 4.36 (2 H, complex), d 3.16 (2 H, complex); ir 1713 cm^{-1}; dipole moment 1.5 D. In this instance the nmr spectrum showed no pronounced change with temperature and it is clear that the six-membered ring in **4b** has lost its mobility and formed a stable chair which is bridged diequatorially by the methylene chain.

2,13-Dibromocyclotridecanone[9] reacted with furan in the presence of zinc–copper couple to give the mobile homotricyclic pair **2c** $\rightleftharpoons$ **3c**. Interestingly, the nmr spectrum could no longer be resolved on going down to $-80°$; on further cooling the compound crystallized from solvent $CFCl_3$. Thus, the activation barrier must be lower than 8 kcal/mol in this case. In solvent CCl_4 the chair conformer **2c** was estimated to be more stable than **3c** by 650 cal/mol, but by only 380 cal/mol in $(CD_3)_2CO$ and $CHCl_3$.[10] Both the diaxially substituted chair **1c** and the skew isomer **6c** were also formed in the reaction.

Finally, cycloaddition of 2,11-dibromocycloundecanone[3] to furan yielded the diaxially bridged nortricycle **3a**, which was frozen as a boat and did not flip to **2a** below 140°, *i.e.*, $\Delta G^{\ddagger} > 22$ kcal/mol. On reduction of the double bond the boat conformation was retained (*cf.* **5a**), but on heating to *ca.* 90° the diequatorially bridged chair **4a** was formed quantitatively and as far as we can tell, irreversibly, since further heating up to 160° did not regenerate the boat derivative **5a**.

In conclusion the series of tricyclic model compounds **2b–c** and **3a–c** seem unique in that they can adopt truly symmetrical boat conformations. Where chair–boat interconversion is possible, the transition state is presumably close to a symmetrical half-boat with five carbon atoms in one plane and involving only small entropy changes.

The reactions described are of synthetic interest as a new annelation procedure and they also yield insight into the geometry of the intermediate allyl cation as well as the ensuing transition state, as we shall discuss in the full paper.

Acknowledgments. We thank Dr. J. E. Anderson for discussions, Professor H. Hellmann of Chemische Werke Hüls for a generous sample of cyclododecanone, Dr. B. Willhalm of Firmenich & Cie, Geneva, for mass spectrometric analyses, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[8] I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 71 (1971).

[9] Prepared from cyclotridecanone and bromine (2 mol equiv) in ether at 0°. Only the high melting isomer, mp 110°, was used.

[10] It is assumed that the vicinal coupling constant of the bridgehead protons is 3.5 Hz in **2c** and 7.5 Hz in **3c**, as observed for **3a** as well as **2b** and **3b**. As chemical shifts coalesce the coupling constants average to the weighted mean of the individual conformers. At 25° in CCl_4 solution the observed coupling constant of the mobile tricyclic was 5.5 Hz (**2c**:**3c** = 3:1) and in $(CD_3)_2CO$ and $CDCl_3$ 6.0 Hz (**2c**:**3c** = 1.9:1). The experimental error of this estimate is probably not greater than ±15%.

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Synthesis and Reactions of Some New Aryldiazo Complexes of Iridium

Sir:

We wish to report a facile synthetic route to a variety of new iridium aryldiazo complexes and to present preliminary information on their characterization. The key compound, $IrCl(ArN_2)(PPh_3)_2^+$ (I),[1] undergoes a variety of interesting reactions with small molecules and ions similar to $IrCl(CO)P_2$[2] and $IrCl(NO)P_2^+$.[3] The presence of the aryldiazo group provides a convenient means for changing the basicity of the diazo ligand and for observing electronic and structural effects on the ligand and metal. ArN_2 has the same amphoteric nature as NO and is a distinctly better π-electron acceptor and poorer σ-electron donor.

Compound I is quickly prepared in one step from $IrCl(CO)(PPh_3)_2$ in 75–85% yields by allowing a chloroform solution of the carbonyl to react with an aroyl azide followed immediately by the addition of an aryldiazonium salt. The reaction

$$IrCl(CO)(PPh_3)_2 \xrightarrow[ArN_2^+PF_6^-]{EtOH,\ ArCON_3} IrCl(ArN_2)(PPh_3)_2^+PF_6^-$$

which is carried out using deoxygenated solvents at room temperature in a dry nitrogen atmosphere, almost certainly involves the initial formation of the dinitrogen complex.[4] Any $ArN_2^+X^-$ may be used when X^- is a noncoordinating anion. Alternatively, anions may be exchanged using a large excess of the respective acid in acetone–water.[5]

Compound I reacts with carbon monoxide, isonitriles, phosphines, arsines, and stibines to form the respective five-coordinate species (Table I). With five coordination occurs a sharp decrease in $\nu(NN)$ by about 200 cm^{-1} for PR_3, AsR_3, and SbR_3 and 350 cm^{-1} for CO and RNC. Though the values of $\nu(NN)$ are somewhat lower for the aryldiazo complexes, they seem to correspond to $\nu(NO)$ for the nitrosyl analogs. By analogy with known nitrosyl structures,[6] tentative coordination geometries, which must be confirmed experimentally, can be assigned: the trisphosphine and bisphosphine arsine complexes are trigonal bipyramids with linear (Ir–N–N) aryldiazo ligands; the bisphosphine isonitrile and carbonyl complexes are square pyramids with bent aryldiazo ligands. Because of the wide range of $\nu(NN)$, we anticipate that the Ir–N–N–Ar linkage may show interesting variations from compound to compound.

Table I

Compound[a]	Appearance	$\nu(NN)$	$\nu(NN)$[b]	$\nu(CO)$ or $\nu(CN)$
$IrCl(PhN_2)P_2^+$	Deep green	1868[c]	1834	
$IrCl_3(PhN_2H)P_2$	Orange-yellow	1404	1397	
$IrCl(PhN_2)P_3^+$	Blood red	1651	1625	
$IrCl(PhN_2)P_2(EtNC)^+$	Pale yellow	1499	1484	2268
$IrCl(PhN_2)P_2(CO)^+$	Yellow	1510	1490	2099
$IrCl_2(PhN_2)P_2(EtNC)$	Orange	1465	1457	2240
$IrCl_2(PhN_2)P_2(CO)$[d]	Orange	1464	1457	2077
$IrCl(NCO)(PhN_2)P_2(CO)$	Orange	1461	1454	2071[e]
$IrCl_2(PhN_2COCH_3)P_2^+$	Orange-yellow	1501	1483	1576[f]

[a] A representative group of the compounds prepared; frequencies given as cm^{-1}; C, H, and N elemental analyses are satisfactory for all compounds; spectra taken in perfluorokerosene and hexachlorobutadiene mulls; anions are always PF_6^-, P = PPh_3. [b] Frequency when terminal nitrogen of ArN_2 is ^{15}N. [c] This is the highest known value except for $RuCl_3(PhN_2)(PPh_3)_2$ where $\nu(NN)$ is 1882 cm^{-1}. [d] Analogous $PPhMe_2$ derivative previously prepared, see A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969). [e] $\nu(NCO)$ = 2260, 1353 cm^{-1}. [f] Tentative assignment.

Compound I also reacts with lithium halides (and pseudo halides) and cyanoethylenes (cyano, *trans*-1,2-dicyano, tetracyano, and triphenylcyano). A stable 1:1 complex is readily isolated with tetracyanoethylene, but the structure of the product is uncertain at this time. I reacts with exactly 1 equiv of LiCl in slightly basic methanol to form an unstable compound analyzing close to $IrCl_2(PhN_2)(PPh_3)_2$. In the presence of excess Cl^- or $CHCl_3$, $IrCl_3(PhN_2H)(PPh_3)_2$ is formed which is the same product resulting from the addition of excess HCl to I; the latter compound cannot be deprotonated using moderately strong bases.

The five-coordinate complexes, $IrCl(ArN_2)P_2L^+$ (L = RNC, CO, P), can be formed either by adding L to $IrCl(ArN_2)P_2^+$ or by adding ArN_2^+ to $IrClP_2L$; both synthetic routes are useful. The orange four-coordinate isonitrile complex, however, is air sensitive and was prepared by carefully adding exact stoichiometric amounts of an isonitrile to the dinitrogen complex; it must be prepared and handled under nitrogen.

The reported compounds are reasonably stable at room temperature except for the five-coordinate complexes with $\nu(NN)$ below 1520 cm^{-1} which are stable in solution for several minutes to several hours and are only slightly more stable in the solid state. Although the decomposition products have not been fully characterized, it appears that similar compounds are prone to undergo ortho metalation on the aryl ring of the diazo group.[7] Using the "blocked" diazonium salt, $2,6-F_2C_6H_3N_2^+$, the unstable five-coordinate compounds show noticeably greater thermal stability.

A variety of six-coordinate complexes, $IrCl(X)(p\text{-}YC_6H_4N_2)(PPh_3)_2(L)$, have been prepared where X = Cl, Br, I, N_3, NO_2, and NCO; Y = F, H, and CH_3; L = CO and EtNC. They are considerably more stable than the similar five-coordinate ones presumably because there is no vacant coordination site on the iridium which could interact with the phenyl ring. The best synthetic route to the six-coordinate complexes involves allowing $ArN_2^+PF_6^-$ to react with $IrClP_2L$ followed by the addition of X^-, although the other route (adding L to I and then immediately X^-) can also be employed. These compounds are undoubtedly 18 electron systems (not 20 electron) and probably possess bent, reactive ArH_2^- moieties. $IrCl_2(PhN_2)(PPh_3)_2(CO)$ reacts with $Et_3O^+BF_4^-$ in CH_2Cl_2 and reversibly with HBF_4 in EtOH to give pale yellow compounds whose elemental analyses and infrared spectra are consistent with the formulations $IrCl_2(PhN_2Et)(PPh_3)_2(CO)^+BF_4^-$ and $IrCl_2(PhN_2H)(PPh_3)_2(CO)^+BF_4^-$.

Compound I does not undergo oxidative addition re-

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(1) Ar = aryl, Ph = phenyl, Me = methyl, Et = ethyl, and P = tertiary phosphine.

(2) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968); J. P. Collman, *ibid.*, **1**, 136 (1968).

(3) C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969); 1459 (1969).

(4) J. P. Collman, M. Kubota, F. D. Vastine, T. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968); J. P. Collman, N. W. Hoffman, and J. W. Hosking, *Inorg. Syn.*, **12**, 8 (1970).

(5) By substituting *tert*-butyl nitrite and concentrated aqueous $HClO_4$, HPF_6, or HBF_4 for the diazonium salt, $IrCl(NO)(PPh_3)_2^+$ can be easily prepared in one step from the carbonyl in 80% yields; this is an improvement on the synthesis given by R. J. Fitzgerald and H. W. Lin, *Inorg. Chem.*, **11**, 2270 (1972).

(6) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci., Phys. Chem.*, **11**, 33 (1972).

(7) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Cahan, and D. Sutton, *J. Amer. Chem. Soc.*, **93**, 1826 (1971); **94**, 645 (1972).

actions as readily as does $IrCl(CO)P_2$.[8] Thus, it reacts relatively slowly with MeI, CF_3I, C_6F_5COCl, $MeSO_2Cl$, $PhCH_2Br$, PhCOCl, and MeSCN to form products which have not yet been fully characterized, but it reacts readily with CH_3COCl and CF_3COCl to form beautiful orange-yellow crystals of the stable 1:1 adducts. Though not conclusive evidence, infrared spectra suggest that the acetyl chloride compound is six coordinate and contains a chelating phenyl acetyl diazene.

$NO^+PF_6^-$ reacts with a methylene chloride solution of I to give an almost quantitative yield of $IrCl(NO)(PPh_3)_2^+$ and the diazonium salt. Thus, NO^+ binds more tightly than PhN_2^+ to Ir(I) by virtue of its better σ-electron donor characteristics. NOCl and Cl_2 react with I to give $IrCl_4P_2$ in good yields. I also reacts rapidly with NO_2^-, BH_4^-, NH_2^-, OH^-, Br_2, I_2, N_2H_4, $P(OPh)_3$, PF_3, MeCN, Et_2S, PhSH, PhC_2H, LiMe, and LiPh; it reacts more slowly with carboxylic acids, water, amines, Me_3SnCl, MeHgCl, Ph_2S_2, Ph_3C^+, and $PhCO^+$. I is soluble in pure methanol and reacts slowly with it; this reaction is very rapid in the presence of MeO^-, but does not take place at all in the presence of H^+. I does not react with trialkyloxonium salts, noncoordinating mineral acids, O_2, Ph_3PO, $BiPh_3$, or Ph_2C_2. Many of the above reactions are being investigated further. In addition, the solid-state structures of several of the aryldiazo complexes discussed here are under study. We anticipate that the synthetic and structural chemistry of these compounds will prove to be diverse and interesting.

Acknowledgments. This research was supported by the Advanced Research Projects Agency of the Department of Defense and by the National Science Foundation through the Northwestern University Materials Research Center. We wish to thank Matthey Bishop, Inc. for the generous loan of iridium.

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(8) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604 (1967); J. P. Collman and C. T. Sears, *Inorg. Chem.*, 7, 27 (1968).

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Absolute Rate Constants for the Reaction of *tert*-Butylperoxy Radicals with Some Meta- and Para-Substituted Toluenes[1]

Sir:

We have previously shown[2] that absolute rate constants for the abstraction of a hydrogen atom from a variety of organic compounds (RH) by a tertiary peroxy radical (t-ROO·)

$$t\text{-ROO}\cdot + \text{RH} \xrightarrow{k_p} t\text{-ROOH} + \text{R}\cdot \qquad (1)$$

can be described by eq 2. This implies that the reactivity of R–H to a particular peroxy radical is governed

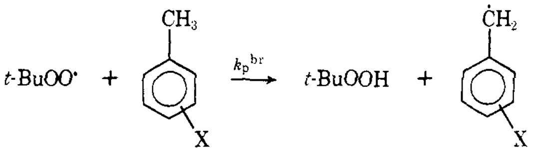
$$\log [k_p/(M^{-1}\ \text{sec}^{-1})] = 15.4 - 0.2D[\text{R–H}] \qquad (2)$$

principally by the strength of the weakest bond in RH, D[R–H].

It has, however, been suggested[3,4] that polar effects may play an important role in determining the reactivity of some substrates. For example, the existence of Hammett $\rho\sigma$ or Brown $\rho\sigma^+$ correlations, with negative ρ values, for meta- and para-substituted toluenes and cumenes has been cited as evidence for the contribution of dipolar structures, such as $ROO^{\delta-}:H\cdot{}^{\delta+}CH_2C_6H_4X$, to the transition state.

The concept of polar effects in H-atom transfer reactions has recently been questioned by Zavitsas and Pinto[5] because of a linear correlation that was obtained between ρ and ΔH for the abstraction of a hydrogen atom from ring-substituted toluenes by Cl·, Br·, t-BuO·, Cl_3C·, and C_6H_5. These workers concluded that ρ depends only on the extent of bond breaking as reflected by ΔH and that differences in the relative reactivities of substituted toluenes to a particular radical are due to differences in D[R–H].

We now report absolute rate constants for the reaction of 13 ring-substituted toluenes with *tert*-butylperoxy radicals in an attempt to determine the importance of polar effects on the H-atom transfer reaction



(3)

These rate constants were determined by the "hydroperoxide method" described in previous papers in this series[6] and are listed in Table I. Plots of log (k_p^{br}/M^{-1} sec^{-1}) against Hammett σ or Brown σ^+ substituent

Table I. Absolute Rate Constants for the Reaction of Some Para- and Meta-Substituted Toluenes with *tert*-Butylperoxy Radicals at 30°

Substituent	k_p^{br}, M^{-1} sec^{-1} [a]
p-Methoxy[b]	0.083
p-Phenoxy	0.066
p-Methyl	0.056
m-Methyl	0.035
None	0.031
p-Chloro	0.030
m-Methoxy[b]	0.027
p-Carbomethoxy	0.025
m-Chloro	0.0185
p-Cyano	0.014
p-Nitro	0.0145
m-Cyano	0.011
m-Nitro	0.0105
p-Acetyl	0.008

[a] Overall propagation rate constant, the values for p- and m-xylene were statistically corrected. [b] Values of k_p^{br} (overall) = 0.0025 and 0.0035 M^{-1} sec^{-1} were found for anisole and p-methoxyanisole, respectively. The k_p^{br} values of p-methoxytoluene and m-methoxytoluene have been corrected for this contribution.

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(1) (a) Absolute Rate Constants for Hydrocarbon Autoxidation. XXIII. (b) Issued as NRCC No. 13198.

(2) S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

(3) (a) G. A. Russell, *J. Amer. Chem. Soc.*, **78**, 1047 (1956); (b) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

(4) J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.*, **46**, 1017 (1968).

(5) A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972).

(6) See ref 2 and references listed therein.