nate phosphine $(CF_3)_2P^{15}NH_2$, **3**.[5] The nmr data for **1** are consistent with a trigonal bipyramidal structure in which the NH_2 groups occupy equatorial positions.[6] The relative sign data which are presented in Table I

Table I. The Signs and Magnitudes for Some Nmr Coupling Constants of **1**, **2**, and **3**

Coupling	J, Hz	$K(10^{20}$ $cm^{-3})^a$	Types of double resonance experiments[b]
	$F_3P(^{15}NH_2)_2$, **1**		
$^{15}N-^{31}P$	-81.54	$+165.34$	
$^{31}P-^{19}F_a{}^c$	-672.08	-146.79	
$^{31}P-^{19}F_e{}^c$	-791.58	-172.89	$^1H-[^{31}P], ^{31}P-[^1H],$
$^{31}P-N-^1H$	$+14.51$	$+2.98$	$^{19}F-[^1H], ^{19}F-[^{19}F]$
$^1H-N-P-^{19}F_a{}^c$	$+20.71$	$+1.83$	
$^1H-N-P-^{19}F_e{}^c$	-1.81	-0.16	
	$F_3P = {}^{15}NP'F'_2$, **2**[d]		
$^{15}N-^{31}P$	-53.20	$+107.5$	$^{31}P-[^{31}P]$
$^{15}N-^{31}P'$	$+93.76$	-189.6	
	$(CF_3)_2P^{15}NH_2$, **3**		
$^{15}N-^{31}P$	$+52.60$	-106.66	See ref 5
$^{31}P-N-^1H$	-14.21	-2.92	

[a] For definition of K see ref 11. [b] See ref 7, 8, and 9. [c] F_a = axial fluorine, F_e = equatorial fluorine in a trigonal bipyramidal structure. [d] See ref 12.

were obtained by a combination of spin tickling,[7] nuclear Overhauser effect,[8] and selective decoupling[9] experiments. All the signs for **1** have been related to a negative sign for the directly bonded $^{31}P-^{19}F$ coupling[10] can therefore be considered absolute.

One noteworthy feature of the data (Table I) is the finding that the sign of the directly bonded coupling, $K_{^{15}NP}$,[11] is negative in **3** and positive in **1**. Furthermore, homonuclear $^{31}P-[^{31}P]$ double resonance experiments on **2** demonstrate that the signs of the two directly bonded $^{15}N-^{31}P$ couplings are different[12] in the same molecule. Negative to positive sign changes have also been observed in the directly bonded $^{13}C-$ ^{31}P[13] and $^{31}P-^{31}P$[14] couplings when the coordination number of phosphorus is increased from 3 to 4 or 5.

(5) A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Commun.* 1491 (1970).

(6) Dynamic nmr studies have established that at 25° (on the nmr time scale): (i) axial–equatorial fluorine positional interchange is slow and (ii) rotation around the N–P bonds is rapid. The four amino protons are therefore coupled equally to the axial or equatorial fluorine ligands at 25°. See E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972).

(7) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

(8) K. Kuhlmann and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **85**, 1010 (1963).

(9) R. Freeman, K. A. McLauchlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, **5**, 321 (1962).

(10) The $^{31}P-^{19}F$ coupling constant has been shown to be absolute negative, see D. L. VanderHart, H. S. Gutowsky, and T. C. Farrar, *J. Chem. Phys.*, **50**, 1058 (1969).

(11) Since the ^{15}N nucleus possesses a negative magnetogyric ratio, comparisons between coupling constants are best made by employing the reduced coupling constant, K_{AB}, which is defined by the equation $K_{AB} = (2\pi/\hbar\gamma_A\gamma_B)J_{AB}$ where γ_A and γ_B are the magnetogyric ratios of nuclei A and B, respectively.

(12) The homonuclear ^{31}P double resonance experiments (Table I) do not yield the absolute signs of the two $^{15}N-^{31}P$ coupling constants. However, by analogy with **1** and **3** $K_{^{15}NP}$ (tetracoordinate) and $K_{^{15}NP'}$ (tricoordinate) are expected to be positive and negative, respectively.

(13) (a) W. McFarlane, *Chem. Commun.*, **58** (1967); (b) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968); (c) H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Commun.*, 671 (1970); (d) R.-M. Lequan, M.-J. Pouet, and M.-P. Simonnin, *J. Chem. Soc., Chem. Commun.*, 475 (1974).

(14) C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, **93**, 1898 (1971), and references therein.

Qualitatively the sign changes in $K_{^{15}NP}$ seem to relate to the changes in hybridization at the phosphorus atom. In **3** and the tricoordinate phosphorus atom of **2** the bonding description is essentially $(3p)^3$ ($\sim0\%$ P(3s) character) while in the tetracoordinate phosphorus atom of **2** and the equatorial plane of trigonal bipyramidal **1** the bonding schemes are sp^3 (25% P(3s) character) and the $3s3p^2$ (33.3% P(3s) character), respectively. Note that as $K_{^{15}NP}$ changes from negative to positive then becomes progressively larger as the per cent of P(3s) character increases. This correlation is understandable in terms of the model of Jameson and Gutowsky[1c] in which increasing the valence s character (*e.g.*, at phosphorus) causes a changeover in the dominant coupling mechanism from an indirect negative (core polarization) interaction to a direct positive (Fermi contact) interaction.

The difference in sign in the $^{31}P-N-^1H$ coupling in **1** and **3** is also of interest. The sign of, *e.g.*, the $^{31}P-C-$ ^1H coupling is also dependent on the phosphorus coordination number; however K_{PCH} changes from positive to negative when the phosphorus coordination number is increased.[15] The sign difference in the equatorial and axial $^{19}F-P-N-^1H$ couplings is also noteworthy since in the analogous phosphorane, $(CH_3)_2PF_3$, both F–P–C–H couplings are positive;[13c] however, it is significant that the equatorial coupling is appreciably smaller than the axial coupling.

(15) (a) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966); (b) A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, **89** (1966); (d) G. Mavel, *Progr. Nucl. Magn. Resonance Spectrosc.*, 1, 251 (1966); (d) W. McFarlane, *Chem. Commun.*, 58 (1967); (e) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, 7, 165 (1968).

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Exciplexes of a Transition Metal Complex

Sir:

Excimer and exciplex formation is a widespread phenomenon for aromatic molecules.[1-3] In the field of transition metal complexes the formation of excimers or exciplexes has been invoked only in a few cases[4-6] and, to our knowledge, excimer or exciplex

(1) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968.

(2) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970.

(3) B. Stevens, *Advan. Photochem.*, 8, 161 (1971).

(4) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, **90**, 7196 (1968).

(5) J. B. Callis, J. M. Knowles, and M. Gouterman, *J. Phys. Chem.*, 77, 154 (1973).

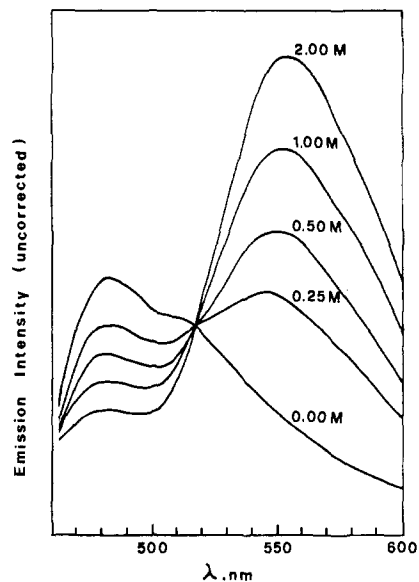(6) G. Sergeeva, A. Chibisov, L. Levshin, and A. Karyakin, *J. Chem. Soc., Chem. Commun.*, 159 (1974).

Figure 1. Luminescence spectra of dimethylformamide solutions of 5×10^{-4} M cis-Ir(phen)$_2$Cl$_2^+$ in the presence of various added concentrations of naphthalene.

Figure 2. Presumable molecular structure of the cis-Ir(phen)$_2$Cl$_2^+$–naphthalene exciplex.

luminescence has never been observed. We report here some results which demonstrate the formation of exciplexes from an excited state of a transition metal complex.

The cis-dichlorobis(1,10-phenanthroline)iridium(III) ion, cis-Ir(phen)$_2$Cl$_2^+$, is photoinert and emits a strong luminescence in deaerated dimethylformamide solution at room temperature.[7] According to Crosby, et al.,[8] this luminescence emission originates from the triplet dπ^* (iridium-to-phenanthroline) charge transfer excited state which is the lowest excited state of the complex and lies at $\sim$21 kK above the ground state.[9] We have found that trans-stilbene (E_T = 17.5 kK) quenches the cis-Ir(phen)$_2$Cl$_2^+$ luminescence in a regular way, with k_{SV} = 150 M^{-1}. Naphthalene (E_T = 21.3 kK) was also found to quench the cis-Ir(phen)$_2$Cl$_2^+$ luminescence ($k_{SV} \sim 2~M^{-1}$, measured at λ_{em} 480 nm), but in this case a new broad structureless emission band with maximum at 560 nm appeared at high naphthalene concentrations (Figure 1). At constant naphthalene concentration, the intensity of the 560-nm band decreased with increasing temperature and at the same time there was a small increase of the emission in the 480-nm region. The 560-nm band was also strongly quenched by oxygen. Under our experimental conditions (cis-Ir(phen)$_2$Cl$_2^+$ = 5×10^{-4} M, naphthalene up to 2 M, excitation wavelength 410 nm) the exciting light was only absorbed by the iridium complex. Moreover, the naphthalene fluorescence and phosphorescence (the latter cannot be observed in DMF solution at room temperature) are expected to occur at much higher energies (E_S and E_T

(7) R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandola, and M. Z. Hoffman, J. Amer. Chem. Soc., submitted for publication.

(8) G. A. Crosby, R. J. Watts, and D. H. W. Carstens, Science, 170, 1195 (1970); J. N. Demas and G. A. Crosby, J. Amer. Chem. Soc., 93, 2841 (1971); R. J. Watts and G. A. Crosby, ibid., 93, 3184 (1971).

(9) The validity of the orbital[10] and spin[11] "labels" of the excited states of metal chelates of this type has recently been questioned.

(10) M. K. DeArmond and J. E. Hillis, J. Chem. Phys., 54, 2247 (1971).

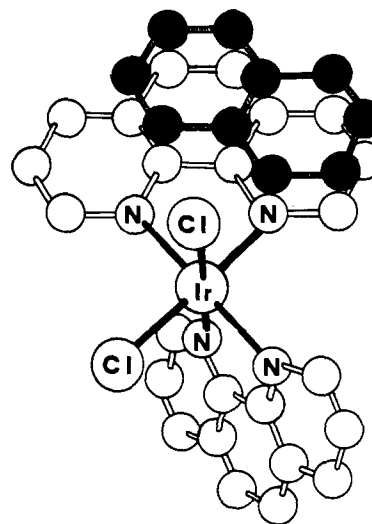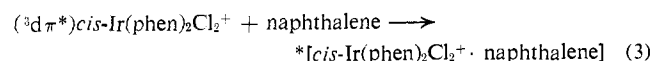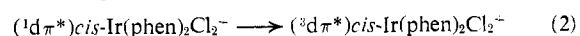(11) G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., J. Amer. Chem. Soc., 96, 629 (1974).

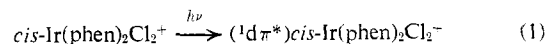for naphthalene are 32.2 and 21.3 kK, respectively[2]), so that there is no doubt that the band with maximum at 560 nm (17.8 kK) is due to a new species which is formed upon excitation of cis-Ir(phen)$_2$Cl$_2^+$ in the presence of ground state naphthalene. Such a new species cannot be a stable photoproduct since the intensity of the 560-nm emission band did not depend on the period of irradiation. Naphthalene has no effect on the cis-Ir(phen)$_2$Cl$_2^+$ absorption spectrum, so that interactions between ground state cis-Ir(phen)$_2$Cl$_2^+$ and ground state naphthalene can also be excluded. Therefore, all the evidence points to the formation of an exciplex between an excited state (most probably, the emitting one) of the complex and ground state naphthalene

$$\text{cis-Ir(phen)}_2\text{Cl}_2^+ \xrightarrow{h\nu} (^1\text{d}\pi^*)\text{cis-Ir(phen)}_2\text{Cl}_2^- \quad (1)$$

$$(^1\text{d}\pi^*)\text{cis-Ir(phen)}_2\text{Cl}_2^- \longrightarrow (^3\text{d}\pi^*)\text{cis-Ir(phen)}_2\text{Cl}_2^- \quad (2)$$

$$(^3\text{d}\pi^*)\text{cis-Ir(phen)}_2\text{Cl}_2^+ + \text{naphthalene} \longrightarrow$$
$$\hspace{4cm} *[\text{cis-Ir(phen)}_2\text{Cl}_2^+ \cdot \text{naphthalene}] \quad (3)$$

The behavior observed on changing naphthalene concentration (Figure 1) or temperature (see above) is just that expected for exciplex formation.[1,2,12,13] A plot of ln (I_{exc}/I_{ir}) vs. $1/T$, where I_{exc} and I_{ir} are the emission intensities of the exciplex at 560 nm and of cis-Ir(phen)$_2$Cl$_2^+$ at 480 nm, respectively, gave a value of about -4 kcal (i.e., about -1.4 kK) for the enthalpy of photoassociation (eq 3).[12,13] Therefore, the repulsion energy between unexcited molecules in the exciplex configuration[12] contributes substantially to the red shift ($\sim$3 kK) of the exciplex band maximum relative to the 0–0 transition of the cis-Ir(phen)$_2$Cl$_2^+$ emission.

Excitation of free phenanthroline in the presence of naphthalene did not cause any new emission; moreover, the phenanthroline fluorescence was not quenched. Since the excited state of the complex is characterized by an increased electron density on the phenanthroline ligands, the major contribution to the exciplex binding energy is presumably due to a charge transfer from a coordinated phenanthroline to naphthalene. The

(12) B. Stevens and M. I. Ban, Trans. Faraday Soc., 60, 1515 (1964).

(13) J. B. Aladekomo and J. B. Birks, Proc. Roy. Soc., Ser. A, 284, 551 (1965).

participation of the t_{2g} metal orbitals in the exciplex bond is also possible.

Scale models of *cis*-Ir(phen)$_2$Cl$_2$⁺ and naphthalene show that there is no steric hindrance for the approach of naphthalene to a phenanthroline ligand in the way shown in Figure 2. One can easily see that there are four almost equivalent configurations of the type shown in the figure. In each of these configurations hydrogen bonding between naphthalene and a chloride ligand can contribute to the stability of the exciplex. The approach of naphthalene to the other side of the phenanthroline ligands is also possible, but in this case two out of the four bonding positions are sterically hindered by the presence of the other phenanthroline ligand.

Preliminary experiments have shown that excited *cis*-Ir(phen)$_2$Cl$_2$⁺ also forms exciplexes with 2-acetonaphthone and that excited *cis*-Ir(5,6-Me$_2$phen)$_2$Cl$_2$⁺ forms exciplexes with naphthalene. We are now carrying out a systematic investigation in order to establish the role played by the metal, ligands, ligand substituents, solvent, etc., in the formation of this new type of exciplexes.

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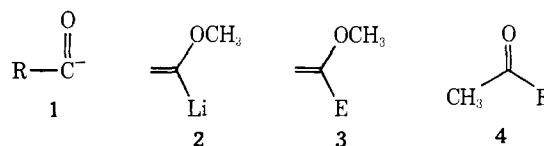Stati Eccitati dei Composti di Coordinazione del C.N.R.
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α-Methoxyvinyllithium and Related Metalated Enol Ethers. Practical Reagents for Nucleophilic Acylation

Sir:

Considerable effort has been recently devoted toward the discovery of useful synthetic equivalents of the acyl anion 1.[1–11] We now communicate our finding that α-

(1) For a review, see D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 8, 639 (1969).

(2) Protected cyanohydrin method: G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, 93, 5286 (1971).

(3) J. E. McMurray and J. Melton, *J. Amer. Chem. Soc.*, 93, 5309 (1971).

(4) Lithiodithiane derivatives: (a) review, D. Seebach, *Synthesis*, 17 (1969); (b) T. Mukaiyama, K. Naraska, and M. Furusato, *J. Amer. Chem. Soc.*, 94, 8641 (1972); (c) E. J. Corey and D. Crouse, *J. Org. Chem.*, 33, 298 (1968); (d) E. L. Eliel and A. A. Hartmann, *ibid.*, 37, 505 (1972); (e) R. J. Cregge, J. H. Herrmann, J. E. Richman, R. F. Romanet, and R. H. Schlessinger, *Tetrahedron Lett.*, 2595 (1973); (f) J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, 2599 (1973); (g) P. Stutz and P. A. Stadler, *Helv. Chim. Acta*, 55, 75 (1972).

(5) Acyl transition metal reagents: (a) E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc.*, 91, 1233 (1969); (b) E. J. Corey and L. S. Hegedus, *ibid.*, 91, 4926 (1969); (c) M. P. Cooke, Jr., *ibid.*, 92, 6080 (1970); (d) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, 94, 1788 (1972); (e) W. O. Siegl and J. P. Collman, *ibid.*, 94, 2516 (1972); (f) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 35, 4183 (1970); (g) Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *ibid.*, 33, 2159 (1968); (h) J. P. Collman and N. W. Hoffman, *J. Amer. Chem. Soc.*, 95, 2689 (1973); (i) J. P. Collman, S. R. Winter, and R. G. Komoto, *ibid.*, 95, 249 (1973).

(6) Metalloaldimines: (a) H. M. Walborsky and G. E. Niznik, *J. Amer. Chem. Soc.*, 91, 7778 (1969); (b) H. M. Walborsky, W. H. Morrison, III, and G. E. Niznik, *ibid.*, 92, 6675 (1970); (c) G. E. Niznik, W. H. Morrison, III, and H. M. Walborsky, *J. Org. Chem.*, 39, 600 (1974); (d) Y. Yamamoto, K. Kondo, and I. Moritani, *Tetrahedron Lett.*, 793 (1974).

methoxyvinyllithium (MVL) (**2**) and related species are readily prepared acyl anion equivalents of considerable synthetic value.[12] The reaction products, *e.g.*, **3**, of these species with electrophiles (E⁺) contain vinyl ethers which may be further elaborated as such or, more usually, can be converted by mild treatment (aqueous methanolic 0.02 N HCl, 25°) to their corresponding carbonyl compounds **4** in high isolated yield. Thus in a typical procedure *tert*-butyllithium (100 mmol, 62.5 ml, 1.6 M in *n*-pentane) was added dropwise to a solution of methyl vinyl ether (9.2 g, 160 mmol) in dry tetrahydrofuran at −65° under nitrogen.[13] After removal of the cooling bath the yellow precipitate[14] redissolved and the solution became colorless between −5 and 0°. This solution which contains quantitatively MVL was cooled to −65° for most reactions, the electrophilic species being added, in solution of tetrahydrofuran, at this temperature. If the vinyl ether product be required, the reaction is quenched (0°) with ammonium chloride solution (20% aqueous). The conversion to the carbonyl compound required reaction with aqueous methanolic 0.02 N HCl (30 min, 20°). The results of reaction of MVL with a selection of different electrophiles are described in Table I, all yields quoted being those of isolated and purified products. As is evident from the table the reaction of **2** with aldehydes and ketones is an efficient route to hydroxyl enol ethers **5** and α-ketols **6**, in excellent yield. The reagent reacts with relatively hindered carbonyl groups, *e.g.*, 17-keto steroids (*cf.* Table I) and it is noteworthy that smooth nucleophilic addition was observed even with substrates which are prone to enolization, *e.g.*, phenylacetone.

MVL is also reactive toward benzonitrile and benzoic acid (0.5 equiv), providing in each instance the hemiprotected diketone **7** and ultimately α-diketone **8**. Along with **7**, a small amount (*ca.* 10%) of the bis

(7) α-Thiosulfoxides: (a) K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 3151 (1971); 1383, 2681 (1972); (b) J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, *ibid.*, 3267 (1973); (c) J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, 3271 (1973); (d) J. L. Herrmann, J. E. Richman, P. J. Wepple, and R. H. Schlessinger, *ibid.*, 4707 (1973); (e) G. Schill and P. R. Jones, *Synthesis*, 117 (1974).

(8) E. J. Corey and J. I. Schulman, *J. Org. Chem.*, 35, 777 (1970).

(9) R. M. Carlson and J. L. Isidor, *Tetrahedron Lett.*, 4819 (1973).

(10) K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, 95, 2694 (1973).

(11) Acyl carbanions themselves generally lack sufficient stability to be useful synthetic intermediates; *cf.* L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. E. Sbarbati, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 95, 8118 (1973); however, recent reports describe species related to 1 which may have discrete lifetimes: U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, 6, 805, 970 (1967); P. Jutzi and F. W. Schröder, *ibid.*, 10, 339 (1971); G. K. Koch and J. M. M. Kop, *Tetrahedron Lett.*, 603 (1974).

(12) While our work was in progress it was reported that ethyl vinyl ether could be metalated by *tert*-butyllithium–tetramethylethylenediamine and the lithiated derivative reacted with benzaldehyde: U. Schöllkopf, personal communication; *cf.* U. Schöllkopf and P. Hänssle, *Justus Liebigs Ann. Chem.*, 763, 208 (1972). Professor G. Büchi of this department has made related observations; G. Büchi and H. Wuest, personal communication.

(13) This is exothermic and should be maintained between −65 and −55°.

(14) This is a complex of *tert*-butyllithium and tetrahydrofuran (2:1); *cf.* F. A. Settle, M. Haggerty, and J. F. Eastham, *J. Amer. Chem. Soc.*, 86, 2076 (1964).