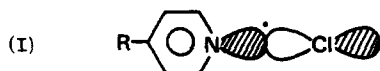


The Pyridine-Chlorine Atom Three-Electron-Bond Intermediate

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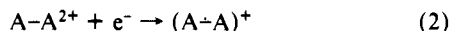
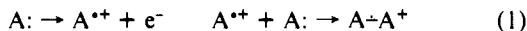
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Recently, Breslow and his co-workers have reported that the three-electron-bonded radical I, formed by reaction between substituted pyridines and chlorine atoms, constitutes a novel, and important, intermediate of a class not widely considered.^{1,2}

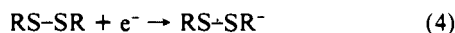
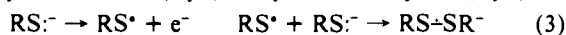


One of our aims (i) is to show that, using the low-temperature matrix-isolation method, we have been able to prepare radical I from pyridine, and to characterize it by EPR spectroscopy with considerable confidence. The other aim (ii) is to stress that there is a wide variety of such three-electron " σ^* " radicals (σ_1^2 , σ_2^1) that have been studied by EPR spectroscopy^{3,4} and electronic spectroscopy.⁵

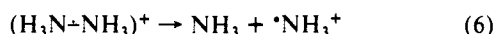
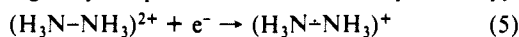
A range of σ^* radicals is given in Chart I. They can be prepared (eq 1) by electron loss from a suitable donor, A:, to give $A^{\bullet+}$ followed by dimerization to give $A-A^{\bullet+}$ or by reaction with B: to give $A-B^{\bullet+}$. The alternative is electron addition to $(A-A)^{2+}$ (eq 2). (The signs are arbitrary; the electron donor is often



anionic.) An important biological example is $RS-SR^-$, formed either by electron loss (eq 3) or by electron capture (eq 4).



Our results suggest that homonuclear σ^* radicals are more stable than most heteronuclear species, and that such radicals involving two first-row elements as the bonding constituents are relatively unstable. We have recently prepared $H_3N-NH_3^{\bullet+}$ via eq 5, but this species readily dissociated at very low temperatures (eq 6),⁶ as judged by temperature-resolved EPR spectroscopy.



The structure envisaged for these σ^* radicals is shown in Figure 1, which indicates the weakening and stretching of the parent σ -bond on electron addition, and the shift of the original $\sigma \rightarrow \sigma^*$ transition to lower energies. In addition to the V_K centers,^{7,8} known halogen atom adducts include the *N*-halosuccinimide radical anions,^{9,10} iodobenzene σ^* anions,¹¹ $N \equiv C-Br^-$ anions,¹² and $HC \equiv C-I^-$ anions.¹³

We have recently shown that when $R_3P^{\bullet+}$ radical cations¹⁴ are formed from R_3P molecules in Freon matrices at 77 K by ionizing

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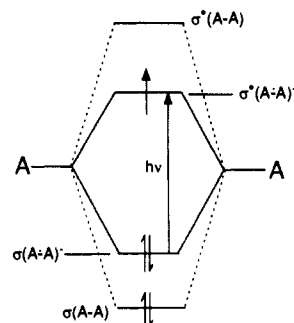


Figure 1. Qualitative energy level diagram for a molecule $A-A$ and its radical anion, $(A-A)^{\bullet-}$, showing how the σ -bond is weakened by the added electron, and the $\sigma \rightarrow \sigma^*$ transition is shifted to low frequencies.

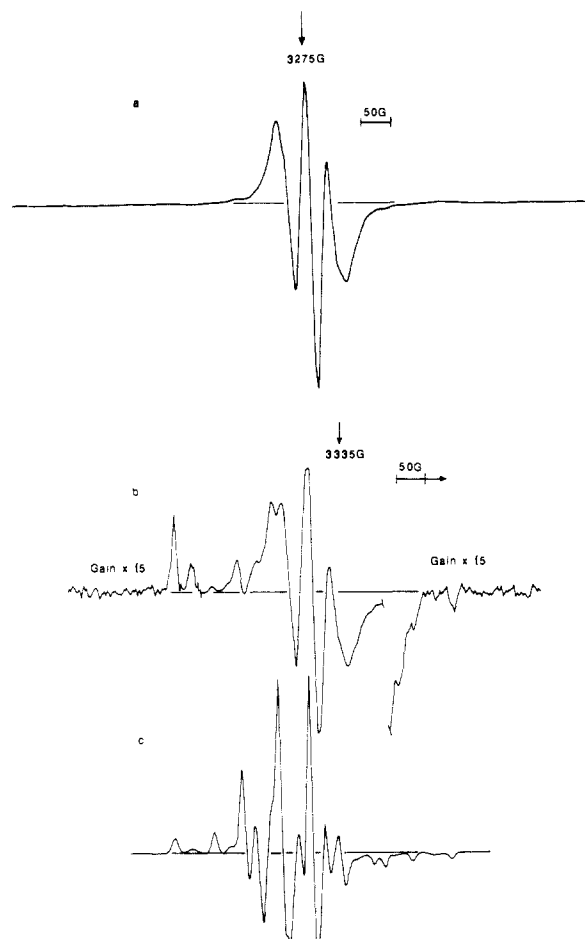
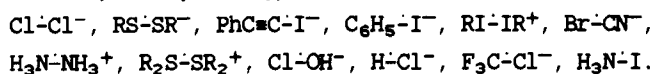
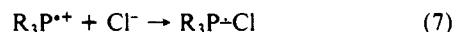


Figure 2. First-derivative X-band EPR spectrum for a dilute (ca. 1:1000) solution of pyridine- d_5 (C_5D_5N) in $CFCl_3$ after exposure to ^{60}Co γ -rays at 77 K: (a) at 77 K, showing features assigned to pyridine radical cations ($C_5D_5N^{\bullet+}$); (b) after annealing to ca. 140 K, showing extra, outer features assigned to the pyridine-chlorine adduct, C_5D_5-Cl ; and (c) simulation of the C_5D_5-Cl spectrum using the data from Table I.

Chart I. A Selection of Three-Electron-Bonded (σ^*) Radicals Studied by EPR Spectroscopy

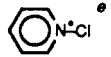
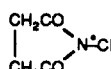


radiation, they can form two types of σ^* radicals on annealing. One is the well-known "dimer" $R_3P-PR_3^{\bullet+}$,¹⁵ and the other is R_3P-Cl , formed by reaction between $R_3P^{\bullet+}$ ions and chloride anions formed by radiolysis (eq 7).¹⁶ Since it is possible to



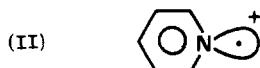
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Table I. EPR Parameters for Various σ^* Radicals Related to the Pyridine-Chlorine Adduct

radical	hyperfine coupling, G ^a			ref	
	A	A _⊥	A _{iso}		
	¹⁴ N	66	42	50	b
	³⁵ Cl	112	22	52	
Ph ₃ P ⁺ Cl ⁻	³¹ P	730	555	613	c
	³⁵ Cl	79	38	52	
	¹⁴ N	68	45	52.7	d
	³⁵ Cl	115	24	54.3	

^aG = 10⁻⁴ T. ^bThis work. ^cAbu-Raqabah, A.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1*, in press. ^dPace, D.; Ezell, K.; Kispert, L. D. *J. Chem. Phys.* **1979**, *71*, 3971. ^eg values of g_x = 2.026, g_y = 2.0313, g_z = 2.003.

generate pyridine radical cations in CFC1₃ at 77 K unambiguously,^{17,18} and since these clearly have the σ -SOMO (II) rather than a π -SOMO, this should be a good system for preparing the pyridine-chlorine adduct.



After generating pyridine cations by radiolysis at 77 K and annealing to ca. 145 K, new EPR features grew in as the (py)^{•+} features were lost. These clearly contain chlorine hyperfine features (Figure 2). From the data (Table I), it can be seen that the maximum hyperfine coupling components for ¹⁴N and ^{35/37}Cl share the same direction, thus establishing that the adduct is a true three-electron-bond unit with the chlorine atom lying in the plane of the ring.

We conclude that σ^* intermediates of this type are of very wide significance and need to be considered in radical reactions whenever one of the reactants or, indeed, the solvent has a suitably localized electron pair available for bonding.

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Characterization of the First η^4 -Vinylketene Metal Complex from the Reaction of a Group 6 Fischer Carbene Complex and an Alkyne[†]

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Premier among the many reactions of Fischer carbene complexes that have found utility in organic synthesis are the benzannulation reactions with alkynes.²⁻⁵ This annulation produces

[†] Dedicated to Professor Leon Stock on the occasion of his 60th birthday.

(1) American Chemical Society Organic Division Rohm and Haas Fellow 1989-1990. William Rainey Harper Fellow 1990-1991.

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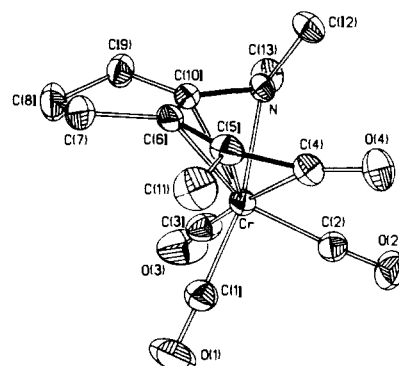
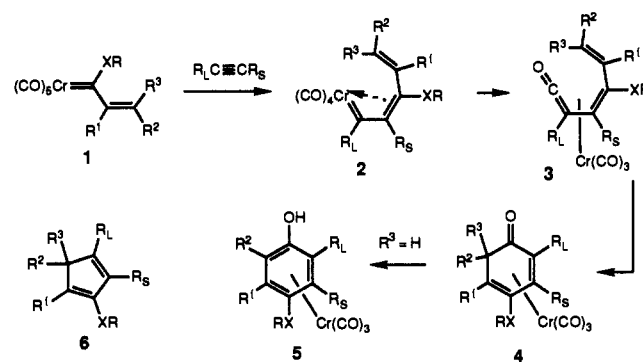


Figure 1. Molecular structure and numbering scheme for **15c** [Cr(CO)₃(C₁₀H₁₅NO)]. Bond lengths (angstroms) and angles (degrees): Cr-C(4), 2.024 (4); Cr-C(5), 2.219 (4); Cr-C(6), 2.200 (4); Cr-C(10), 2.130 (4); Cr-N, 2.194 (3); O(4)-C(4), 1.215 (4); C(4)-C(5), 1.430 (5); C(5)-C(6), 1.424 (6); C(6)-C(10), 1.404 (5); C(10)-N, 1.421 (4); O(4)-C(4)-C(5), 136.0 (4); C(4)-C(5)-C(6), 122.7 (3); C(5)-C(6)-C(10), 126.0 (3); C(6)-C(10)-N, 119.9 (3).

Scheme 1



either the cyclohexadienones **4**⁵ or 4-alkoxyphenols **5**^{3,4} and has provided unique strategies for the synthesis of a number of natural products (Scheme 1). This reaction has long been proposed⁶ to involve an η^4 -vinylketene complex of the type **3** as the penultimate intermediate.^{7,8} Although a number of η^4 -vinylketene complexes are known for various metals, there are no examples for chromium and no examples for d⁶ complexes of the group 6 metals.⁹⁻¹² We

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