Figure 1. Localized molecular orbitals in BH_2F, BF_2H, BF_3, B_2F_4, BF_2NH_2, BF, and B_4F_4.

benzene,[7] for the preference of LMO's, particularly in Boys' method, for *equivalent* orbitals (τ-like) over a σ-π description. For instance, Edmiston-Ruedenberg (ER)[8] localization of BH_2F results in a bond model displaying σ-π separation and not the equivalent orbital description of the Boys localization (Table I).

The LMO valence structures obtained by Boys' procedure are illustrated in Figure 1. The solid line originates at the atom donating an electron pair and becomes dotted toward the atom which is electron deficient, in order to indicate the bond polarity. The exclusion principle is not violated here inasmuch as only fractions of atomic orbitals are usually employed at an atom for an apparent excess of bonds and lone pairs if present. We call these bonds fractional.[9] This (Boys) LMO description is an equivalent alternative to the usual resonance description, including back-donation of π electrons from lone pairs of F into vacant atomic or molecular orbitals on B.[6] The procedure is objective in its indication of the best single valence structure for electron-pair bonding. The bonding reported here may be typical of a large class of both inorganic and organic[10] molecules which contain lone pairs. For example, the B–N bond in BF_2-NH_2 (Table I) is a highly polarized double bond. Thus electron donation of lone pairs can occur whenever there is a sufficient electron deficiency on a neighboring atom. Moreover, the bonding described here is not restricted to B–F bonds.

Finally, as noted above, the ER localization procedure may show preference for a σ-π description rather than a τ-bond description, as illustrated by the ER localization of BH_2F. An objective preference for the ER method over the Boys method (or *vice versa*) requires some firm experimental or theoretical basis. In $1,2$-$C_2B_4H_6$, where the two methods also give different results (a "σ, π" vs. a "τ" description[4]), we observe that the ER result yields an *idealized*[11a] three-center bond structure which gives more nearly neutral

atoms.[11b] For the molecules presented here a reason for choice is not so clear, and we accept at present both descriptions of the bond models for these molecules. We note that both the ER and Boys localization procedures indicate the participation of lone pairs in bonding. The only ambiguity that remains is whether the actual bonding in the molecule is better described as σ-π or as τ bonding.

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Alkyl- and Arylthioiridium(I) Complexes

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Monomeric thioalkyl and -aryl complexes of transition metals are uncommon because of the ready facility for sulfur bridge formation to occur, leading to the isolation of dimers rather than monomers. A number of substituted thioiridium(I) complexes have been recently reported, although in each case the method of preparation appeared to be specific for the compound in question and the authors made no claims as to the generality of the synthetic procedure. The monomeric complex $Ir(C_6F_5)CO(PPh_3)_2$ has been prepared by treating $IrClCO(PPh_3)_2$ with $TlSC_6F_5$[2] or $AgSC_6F_5$.[3] A similar metathetical replacement reaction with $AgSCF_3$ has been used in the synthesis of $Ir(SCF_3)CO$-$(PPh_3)_2$.[4] The nonfluorinated thioiridium(I) complex Ir-$(SH)CO(PPh_3)_2$ has been reported and can be prepared by treating $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ with either sodium sulfide or H_2S.[5] In view of this recent interest in the synthesis of substituted thioiridium(I) complexes of the type $Ir(SR)CO(PPh_3)_2$, we now describe a general method for the preparation of such compounds for a wide range of functional groups R.

Results and Discussion

We have found that the compounds $Ir(SR)CO(PPh_3)_2$ for the range of R groups Et, *i*-Pr, *n*-Bu, Cy, Ph, and *p*-tol can be conveniently prepared by a single general method. These compounds are bright yellow solids and give monomeric solutions in benzene. They are very soluble in benzene and halocarbon solvents and slightly soluble in ether and lower alcohols. The compounds are prepared by the oxidative ad-

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Scheme I. Reaction Sequence for the Synthesis of
Thioiridium(I) Complexes

$$\text{IrClCO(PPh}_3)_2 \xrightleftharpoons{\text{RSH}} \text{IrHCl(SR)CO(PPh}_3)_2 \xrightarrow{\text{base}} \text{Ir(SR)CO(PPh}_3)_2$$
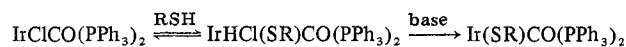
Table I. Infrared Spectral Data for Compounds IrHCl(SR)CO(PPh$_3$)$_2$^{a}

R	ν_{IrH}, cm^{-1}	ν_{CO}, cm^{-1}	R	ν_{IrH}, cm^{-1}	ν_{CO}, cm^{-1}
Et	2240	2045	Cy	2260	2045
i-Pr	2250	2040	Ph[6]	2263	2029
n-Bu	2240	2045	*p*-tol	2259	2030

^{a} The values are accurate to within ±5 cm^{-1}.

Table II. Analytical Data for Compounds Ir(SR)CO(PPh$_3$)$_2$

	% C		% H		Mol wt (C$_6$H$_6$)	
R	Calcd	Found	Calcd	Found	Calcd	Found
Et	58.1	57.9	4.38	4.27	805	794
i-Pr	58.6	57.9	4.55	4.49	819	823
n-Bu	59.0	58.3	4.71	4.86	833	835
Cy	60.1	59.3	4.81	4.83	859	840
Ph	60.5	59.6	4.13	4.13		
p-tol	60.9	60.3	4.30	4.19	867	840

Table III. Spectral Data for Compounds Ir(SR)CO(PPh$_3$)$_2$

R	ν_{CO}, cm^{-1}	τ, ppm	J, Hz
Et	1945	9.48 (Me), 7.97 (CH$_2$)	7.0
i-Pr	1940	9.55 (Me)	6.5
n-Bu	1952	7.9, 9.2 (multiplets)	
Cy	1955	9.0 (multiplets)	
Ph	1950		
p-tol	1950		

dition of RSH to IrClCO(PPh$_3$)$_2$, followed by strong base elimination of HCl. The intermediate hydro complexes IrHCl(SR)CO(PPh$_3$)$_2$, which are unstable to spontaneous reductive elimination of RSH, have been characterized by ir spectroscopy (Table I). However, when these compounds are suspended in methanol and treated with excess of a methanolic solution of NaOMe, reductive elimination of HCl occurs and the compounds Ir(SR)CO(PPh$_3$)$_2$ are formed. The reaction proceeds readily with other strong bases, and NaOH, 1,5-diazabicyclo[4.3.0]non-5-ene, and potassium 2,6-di-*tert*-butyl phenoxide have been successfully used. The reduction of IrHCl(SPh)CO(PPh$_3$)$_2$ to Ir(SR)CO(PPh$_3$)$_2$ fails with ammonia, triethylamine, pyridine, and 1,8-bis(dimethylamino)-naphthalene. The synthetic procedure with strong bases can be carried out without the isolation of hydroiridium(III) intermediates, since the preparation of Ir(SR)CO(PPh$_3$)$_2$ can be accomplished from IrClCO(PPh$_3$)$_2$ by initial treatment with PhSH followed by NaOMe. Our procedure was unsuccessful for the synthesis of Ir(S-*t*-Bu)CO(PPh$_3$)$_2$ probably because of the failure of the initial oxidative addition step to proceed to any significant extent.

These compounds irreversibly add oxygen to form Ir(SR)-CO(O$_2$)(PPh$_3$)$_2$, which show diagnostic bands in the ir spectrum in the region of 1990 and 840 cm^{-1}. The spectra of the dioxygen complexes show no new bands at 1050, 1300–1350, or 1140 cm^{-1} for the oxidation of sulfur to a coordinated sulfoxide or sulfone. The sulfur ligand is removed with strong acid since treating Ir(SPh)CO(PPh$_3$)$_2$ with HCl gives IrHCl$_2$(CO)(PPh$_3$)$_2$.

The reaction sequence for the formation of these iridium-(I) complexes is shown in Scheme I. The stereochemistry of IrHCl(SPh)CO(PPh$_3$)$_2$ is reported to have a geometry with H and Cl mutually trans,[6] which suggests that the reductive elimination of the strong acid must occur from this stereochemical arrangement. It is probable that in the basic medi-

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um there is also removal of RSH; however this would form NaSR which would undergo metathetical replacement with IrClCO(PPh$_3$)$_2$ in the time duration of the reaction. The proportion of each acid eliminated cannot be estimated since the final product is solely Ir(SR)CO(PPh$_3$)$_2$, and the ir spectra show no bands in the region of 315 cm^{-1} for the Ir–Cl stretch.

In conclusion it may be stated that this synthetic procedure is a useful general method for the preparation of monomeric alkyl- and arylthioiridium(I) complexes in good yield.

Experimental Section

Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz. Molecular weights were measured on a Hitachi Perkin-Elmer Model 115 vapor phase osmometer as solutions in benzene. The benzene solutions were prepared with the careful exclusion of air. The syringe system of the osmometer was purged with nitrogen in order to maintain the solutions in an oxygen-free atmosphere. At the completion of the measurements the solutions were the original bright yellow color and not the orange color of the oxygen complex. The equilibration time of the thermistor system is 2 min, and the solutions are air stable for significantly longer periods than this. As a further check on the validity of the molecular weight measurements we determined the value for Ir(S-*p*-tol)CO(O$_2$)(PPh$_3$)$_2$. The found value was 871 which shows an increase of 31 over the value for Ir-(S-*p*-tol)CO(PPh$_3$)$_2$. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrometer as Nujol mulls and all operations were carried out in an inert atmosphere.

Method of Preparation of the Complexes. To a suspension of IrClCO(PPh$_3$)$_2$ in benzene was added an excess of the appropriate thiol. The reaction mixture became homogeneous and then IrHCl-(SR)CO(PPh$_3$)$_2$ slowly precipitated. The solid was filtered and quickly transferred into dry methanol, and a solution of NaOMe was added. After 48 hr the bright yellow complex was filtered with the careful exclusion of air. The complex was washed with dry methanol and ether, dried *in vacuo*, and stored in evacuated ampoules. The yield was essentially quantitative. As a representative example, the *p*-tol derivative was prepared using IrClCO(PPh$_3$)$_2$ (1.00 g) and *p*-toluenethiol (0.162 g) in benzene (20 ml). After 24 hr the complex obtained was reduced with sodium (0.35 g) in methanol (10 ml) by the addition of this solution to IrHCl(S-*p*-tol)CO(PPh$_3$)$_2$ in methanol (10 ml). The analytical and spectral data for the complexes are shown in Tables II and III, respectively.

The complexes Ir(SR)CO(O$_2$)(PPh$_3$)$_2$ were obtained by allowing a solution of the iridium(I) compound in oxygen-saturated benzene to stand for 24 hr at room temperature.

Registry No. IrClCO(PPh$_3$)$_2$, 14871-41-1; IrHCl(SEt)CO(PPh$_3$)$_2$, 51935-87-6; IrHCl(S-*i*-Pr)CO(PPh$_3$)$_2$, 51935-88-7; IrHCl(S-*n*-Bu)CO-(PPh$_3$)$_2$, 51935-89-8; IrHCl(SCy)CO(PPh$_3$)$_2$, 51935-90-1; IrHCl(S-*p*-tol)CO(PPh$_3$)$_2$, 52019-99-5; Ir(SEt)CO(PPh$_3$)$_2$, 51935-91-2; Ir(S-*i*-Pr)CO(PPh$_3$)$_2$, 51935-92-3; Ir(S-*n*-Bu)CO(PPh$_3$)$_2$, 51935-93-4; Ir-(SCy)CO(PPh$_3$)$_2$, 51935-94-5; Ir(SPh)CO(PPh$_3$)$_2$, 51935-95-6; Ir-(S-*p*-tol)CO(PPh$_3$)$_2$, 51935-96-7.

Nucleophilic Substitution on Sulfur. Reactions of S-Methyl-S-phenylsulfiminium Ion with Iodide and Thiourea

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Several reactions involving nucleophilic substitution at sul-