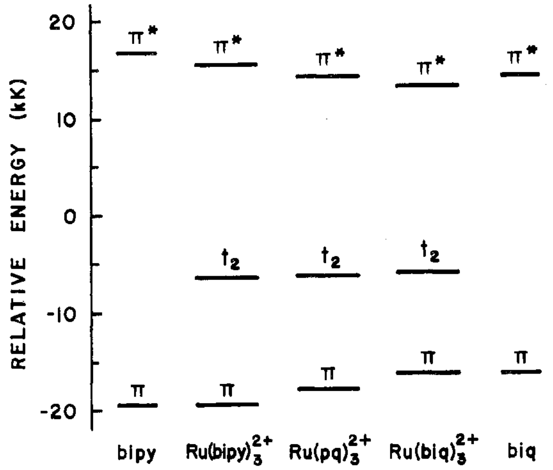

Figure 3. Relative orbital energies of ligands and ruthenium(II) complexes.

be determined from the first intense absorption band in the uv spectra of the complexes ($[Ru(bpy)_3]^{2+}$, 34 930 cm^{-1}; $[Ru(biq)_3]^{2+}$, 29 590 cm^{-1}) assuming that this band is due to a jump of an electron from the last occupied π orbital of the ligand to the first empty one, i.e., a π–π^* transition. The position of the metal t_2 orbital can then be determined from the energy of the charge-transfer (t_2–π^*) absorption band observed in the visible region. The results for the ruthenium complexes are plotted in Figure 3. Since HMO calculations are not available for pq, its HOMO is arbitrarily placed between that of bpy and biq and the relative energies of the other orbitals are calculated as for the bpy and biq complexes.

Three observations concerning Figure 3 can be made. First, the energy difference between the π and π^* levels is less for the biq complex than for the bpy complex, a result which is not surprising in view of the expected additional π-electron delocalization in biquinoline. Second, the energy of the t_2 orbital is higher in the biq complex than in the bpy complex, as would be expected if there is a decrease in the ligand field strength as a result of the increased metal–ligand bond distance caused by steric hindrance in the benzo-substituted complex. Presumably the metal e* orbital is lowered by the weaker field but still remains higher than or equal to the π^* orbital since no d–d transitions (t_2–e*) are observed at low energies in the absorption spectra. Third, the red shift in the CT absorption band results from both a lowering of the π^* level and a raising of the t_2 level but appears to result mainly from the downward shift of the π^* orbital. This conclusion is further substantiated by the fact that only slight shifts (100–300 cm^{-1}) of the CT bands are observed in ruthenium and osmium complexes with 6-methyl-2,2′-bipyridine and 6,6′-dimethyl-2,2′-bipyridine,[22] where a comparable amount of steric hindrance is expected.

The luminescence spectra of the pyridylquinoline and biquinoline complexes are very similar to those of the bipyridine complexes[10-13] with a 1200–1300 cm^{-1} vibrational progression observed on the spectra of all of the complexes. The 1900–3200 cm^{-1} red shift in the energy of the 0–0 bands of pq and biq complexes compared to the emission bands of the corresponding bpy complexes (Table I) parallels the red shift of the absorption charge-transfer bands. Again, this is a much larger shift than that observed (500–800 cm^{-1}) in the emission spectra of methyl- and phenyl-substituted bipyridine complexes.[16-18]

As previously described the CT absorption and emission bands of bis(diquinolylpyridine) (dqp) complexes of ruthenium and osmium are red shifted compared to those of the analogous complexes of terpyridine.[1] Considering the complexes of all three ligands, pq, biq, and dqp, the magnitude of the red shift increases in the order pq < dqp < biq. As more quinoline groups are added to the complex, there is a greater decrease in the energy of the π^* level and a greater red shift of the CT absorption and emission bands.

In view of the general interest in $Ru(bpy)_3{}^{2+}$, $Os(bpy)_3{}^{2+}$, and $Ir(bpy)_3{}^{3+}$ as photosensitizers[23] the relatively large shifts in the absorption and emission spectra brought about by benzo substitution of 2,2′-bipyridine may make pq and biq useful ligands for designing luminescent complexes which will further increase the range of available donor energies. It has been suggested that phenyl substitution on bipyridine be used as a "fine-tuning" device for the design of a series of complexes with slightly modified optical properties.[18] Along this line then, benzo substitution could be regarded as a "coarse-tuning" device to produce large shifts in absorption and emission spectra without changing the basic nature of the transitions responsible for the spectra (as would be the case with a "rough-tuning" device[18]). Additional "fine-tuning" could be possible by the use of phenyl- or methyl-substituted pyridylquinolines and biquinolines.

Acknowledgment. Support of this work by the Robert A. Welch Foundation, Grant Z-449, is gratefully acknowledged.

Registry No. $[Ru(pq)_3](ClO_4)_2$, 60451-54-9; $[Ru(biq)_3](ClO_4)_2$, 60451-56-1; $[Os(pq)_3](ClO_4)_2$, 60451-58-3; $[Os(biq)_3](ClO_4)_2$, 60451-60-7; pq, 7491-86-3; biq, 119-91-5.

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Convenient Nonphotolytic Route to Substituted Carbonyl Anions of Vanadium, Niobium, and Tantalum

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Received March 8, 1976

AIC60176J

Substitution of phosphines and other ligands for carbon monoxide in metal carbonyl anions provides substituted carbonyl anions which are often significantly more basic and nucleophilic than the corresponding binary carbonyl anion.[1-3]

Consequently, the substituted species are valuable reagents for the synthesis of new classes of organometallic compounds. This is particularly true for group 5 carbonyl chemistry since $M(CO)_6^-$ (M = V, Nb, Ta) are either unreactive or generally yield much less thermally stable derivatives than the corresponding pnicogen-substituted anions.[4,5]

Substituted metal carbonyl anions have been obtained by reduction of corresponding metal carbonyl dimers, metal carbonyl halides, or metal carbonyl hydrides, substitution of anionic species into neutral metal carbonyls,[2,6] and direct photosubstitution of neutral ligands into metal carbonyl anions.[5,7] The last route has been the only practical method for the synthesis of substituted metal carbonyl anions of vanadium, niobium, and tantalum because of the inaccessibility of suitable halides, hydrides, or neutral carbonyls for reduction.[7] However, the existence of quite oxidatively, thermally, and solvolytically stable triphenylstannyl derivatives of such anions[4,5] suggested that they could provide a useful alternative route to substituted carbonyl anions which does not require photolysis. In this paper we describe the results of this study.

Experimental Section

General Procedures and Materials. All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed by using standard Schlenk apparatus. Reagent grade tetrahydrofuran was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere. With exceptions noted below, all reagents and other solvents were obtained from commercial sources and used without further purification. Tetraethylammonium salts of substituted carbonyl anions of vanadium, niobium, and tantalum were prepared by published procedures.[5,7] Ir spectra were recorded on a Perkin-Elmer 237B spectrometer. Solution spectra were obtained in sealed sodium chloride cells equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glovebox with essentially complete exclusion of air. All reductions were carried out under the same conditions and will be illustrated by that of $Ph_3SnV(CO)_4dppe$ (dppe = $Ph_2PCH_2CH_2PPh_2$).

Synthesis of $[Et_4N][V(CO)_4dppe]$ from $Ph_3SnV(CO)_4dppe$. A solution of $Ph_3SnV(CO)_4dppe$ (0.165 g, 0.18 mmol) in 15 ml of THF was treated with 1.8 mmol of sodium (4.1 g of 1% sodium amalgam) with stirring. Within 0.5 h the solution changed from yellow to orange-red, the characteristic color of $V(CO)_4dppe^-$. After 4 h the reduction was complete and the amalgam was separated from the solution via a stopcock attached to the side of the flask. Subsequently, the THF was evaporated to dryness. The resulting solid was dissolved in the minimum amount of ethanol (ca. 14 ml; the white hexaphenylditin is only slightly soluble in this solvent) to give a turbid solution. Filtration of the latter through a medium-porosity fritted disk yielded a clear orange-red solution which gave an immediate precipitate on addition of 0.12 g (0.72 mmol) of tetraethylammonium chloride. Ethanol was evaporated completely from the solid which was subsequently washed with water (2 × 10 ml) to remove excess tetraethylammonium chloride. The solid was dried in vacuo and washed with benzene–heptane (1:1 v/v, 2 × 10 ml) to remove additional hexaphenylditin. A clear deep red solution was obtained upon dissolving the dry solid in 12 ml of acetone. After addition of 3 ml of heptane, the solution was slowly evaporated to dryness whereupon deep red crystals formed. These were filtered, washed with pentane (1 × 5 ml), and dried to give 0.121 g (97% yield) of product which gave a Nujol mull infrared spectrum identical with that of an analytically pure sample of $[Et_4N][V(CO)_4dppe]$. Also, the solid filtered off from the ethanol dissolution step proved to have a mull spectrum identical with that of hexaphenylditin.

Synthesis of $Ph_3SnV(CO)_4triphos$. Combined as solids and dissolved in 40 ml of benzene, equivalent amounts (2.40 mmol) of $CH_3C(CH_2PPh_2)_3$ (triphos)[20] (1.50 g), Ph_3SnCl (0.93 g), and $Na(diglyme)_2[V(CO)_6]$ (1.23 g) failed to react until 50 ml of water was added. The benzene layer turned orange, and 7 days later a yellow solid was obtained on solvent removal. After purification through a 6-cm column of silica gel, a methylene chloride solution of the residue was evaporated to dryness. One recrystallization from 50 ml of CH_2Cl_2–12 ml of heptane provided a shiny yellow, analytically pure product (1.50 g, 55% yield; decomposes above 125 °C). Anal. Calcd for $C_{63}H_{54}O_4P_3SnV$: C, 67.14; H, 5.08. Found: C, 66.51; H, 4.78. The osmometric molecular weight in benzene was 1127 (calcd 1138). Infrared spectra of the product in the carbonyl stretching region are consistent with a disubstituted tetracarbonyl structure and are virtually superimposable with corresponding spectra of $Ph_3SnV(CO)_4diars$ (diars = o-$(Me_2As)_2C_6H_4$)[5] and $Ph_3SnV(CO)_4dppe$[4] (ν(CO) for $Ph_3SnV(CO)_4triphos$ in Nujol as mull 1964 (w), 1879 (m), 1862 (s), 1850 (s) cm^{-1}). Chemical evidence for the presence of an uncoordinated phosphine in $Ph_3SnV(CO)_4triphos$ was obtained by treating it with 1 equiv of CH_3I which provided ionic $[Ph_3SnV(CO)_4(PPh_2CH_2)_2C(CH_2PPh_2CH_3)]I$, having essentially the same ν(CO) pattern as that of the reactant.[19]

Synthesis of $[Et_4N][V(CO)_4triphos]$ from $Ph_3SnV(CO)_4triphos$. The triphenylstannyl compound (1.00 g) readily dissolved in 20 ml of THF, giving a yellow solution. Excess 1% Na in Hg (3 ml) caused a color change to deep red. After 6 h reduction was nearly complete; however, even after addition of more amalgam (3 ml) and 17 h of further agitation there remained a weak spike at 1860 cm^{-1} due to reactant. The deep red solution was filtered and evaporated to dryness. Crude orange $Na[V(CO)_4triphos]$ was metathesized in ethanol with a fourfold excess (0.77 g) of Et_4NBr. The bright orange Et_4N^+ salt was recrystallized from 50 ml of acetone–5 ml of 1-butanol, following extensive (5 × 20 ml) H_2O washings to remove NaBr and Et_4NBr. Mull and solution infrared spectra were virtually identical with those of $Et_4N[V(CO)_4dppe]$ (ν(CO) in THF 1903 (s), 1804 (vs), 1792 (sh), 1720 (s) cm^{-1}; mp 209–211 °C dec). Anal. Calcd for $C_{53}H_{59}NO_4P_3V$: C, 69.35; H, 6.48. Found: C, 69.77; H, 6.12.

Reduction of Other Triphenylstannyl Derivatives. Reductions of $Ph_3SnV(CO)_5PPh_3$,[4] $Ph_3SnV(CO)_4diars$,[5] $Ph_3SnV(CO)_4dmpe$ (dmpe = $Me_2PCH_2CH_2PMe_2$),[5] $Ph_3SnTa(CO)_5PPh_3$,[4] and $Ph_3SnNb(CO)_4dppe$[4] were also carried out in THF and were monitored by infrared spectra in the ν(CO) region. All were shown to proceed to completion although isolation of the salts was not attempted as in the above reduction of $Ph_3SnV(CO)_4dppe$. Times required for complete reduction were variable with $Ph_3SnV(CO)_5PPh_3$, $Ph_3SnTa(CO)_5PPh_3$, and $Ph_3SnNb(CO)_4dppe$, requiring less than 12 h. However, $Ph_3SnV(CO)_4diars$ and $Ph_3SnV(CO)_4dmpe$ required 16 and 100 h, respectively, for complete reduction at room temperature.

Results and Discussion

Sodium amalgam reduction of triphenylstannyl derivatives of substituted group 5 metal carbonyls in tetrahydrofuran provides essentially quantitative yields of the corresponding substituted carbonyl anions which may be used in situ for the preparation of other organometallic compounds or isolated as tetraethylammonium salts as described in the Experimental Section. Product studies have shown that the reduction process occurs according to the equation (illustrated with $Ph_3SnV(CO)_4dppe$)

$$Ph_3SnV(CO)_4dppe + Na \rightarrow Na^+V(CO)_4dppe^- + {}^1/_2(Ph_3Sn)_2$$

Previous chemical and electrochemical studies on reductions of other triphenylstannyl derivatives of metal carbonyls have shown essentially identical behavior, i.e.[9]

$$e^- + Ph_3SnM \rightarrow \underset{\substack{\downarrow \\ {}^1/_2(\text{dimer})}}{Ph_3Sn\cdot} + M^-$$

Since the triphenyltin group homolytically cleaves to yield hexaphenylditin, which is not reduced by excess sodium amalgam, the presence of the rather unreactive tin product will not interfere with most reactions of the substituted carbonyl anion with electrophilic species. Metathesis of the sodium salt with tetraethylammonium bromide provides a tetraethylammonium salt in high yield, free of hexaphenylditin.

This reduction process is particularly useful for the preparation of $M(CO)_4dppe^-$ and $M(CO)_5Ph_3P^-$ (M = Nb, Ta) and presumably other related anions since the corresponding triphenylstannyl derivatives are prepared in high yields (~70–90%) by the rapid reaction of Ph_3SnCl and $M(CO)_6^-$ in the presence of the appropriate phosphine.[4] By contrast,