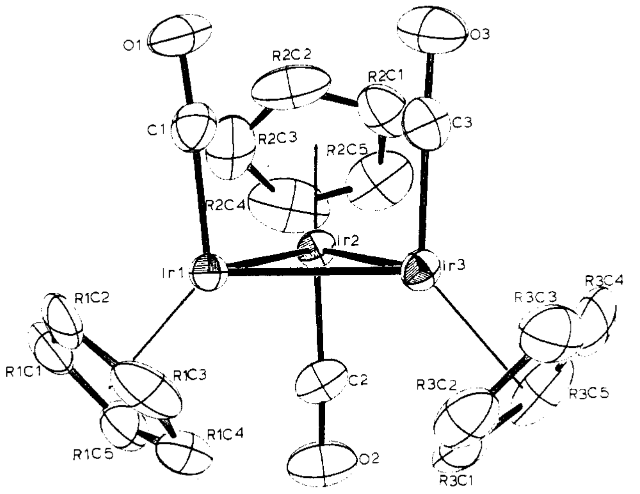


Figure 1. Perspective view of the C_s-$Cp_3Ir_3(CO)_3$ molecule.

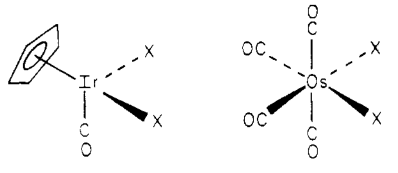
nonbonded repulsions between the two nearly parallel carbonyl ligands. Note that the configuration around Ir(1) (or Ir(3)) is that of a CpIr(CO) complex of a pseudo-ethylene $Cp_2Ir_2(CO)_2$ moiety. This suggests an abvious, though as yet experimentally unexamined, route for the formation and/or decomposition of C_s-$Cp_3Ir_3(CO)_3$.[11]

Under conditions in which it would normally decompose, $CpIr(CO)H_2$ is stabilized by a hydrogen atmosphere. Furthermore, $CpIr(CO)D_2$ under an atmosphere of H_2 is transformed into $CpIr(CO)H_2$. These observations support the equilibrium shown in eq 1. The role of the coordinating

$$CpIr(CO)H_2 \rightleftarrows CpIr(CO) + H_2 \qquad (1)$$

solvent in the decomposition of $CpIr(CO)H_2$ may be seen as a trapping agent to form a "lightly stabilized" species CpIr(CO)S,[12] which facilitates H_2 loss from solution and ultimate formation of $Cp_3Ir_3(CO)_3$. The reactive intermediate CpIr(CO) or CpIr(CO)S is trapped by stronger donors to produce the stable, isolable compounds CpIr(CO)L (L = PPh_3,[13] $PPhMe_2$,[14] CN-*t*-Bu,[14] CO) in good yields. $CpIr(CO)_2$, which is known to be basic,[15] also works well as a trapping agent and forms $Cp_2Ir_2(CO)_3$.[16] Furthermore, decomposition of $CpIr(CO)H_2$ in the presence of benzaldehyde produces benzene and $CpIr(CO)_2$ (as well as $Cp_3Ir_3(CO)_3$), presumably via CpIr(CO)(C(O)Ph)H and CpIr(CO)(Ph)H.[4]

Upon treatment of $Cp_3Ir_3(CO)_3$ with $PPhMe_2$ at increasingly higher temperatures, no reaction occurs until ca. 140 °C (refluxing xylene). The only product is the mononuclear derivative $CpIr(CO)PPhMe_2$. Similarly, at the same temperature in the presence of excess ^{13}CO, only $CpIr(^{13}CO)_2$ is formed[17] and recovered $Cp_3Ir_3(CO)_3$ is unlabeled. This preference for metal-metal bond scission over carbonyl substitution in $Cp_3Ir_3(CO)_3$ parallels the preference for dihydrogen elimination over carbonyl loss from $CpIr(CO)H_2$ (see I). In



I, X_2 = H_2, $Cp_2Ir_2(CO)_2$ II, X_2 = H_2, $Os_2(CO)_8$

contrast the electronically equivalent pair of molecules $Os_3(CO)_{12}$ and $H_2Os(CO)_4$ (see II) show preferential dissociation of carbon monoxide.[18] The difference in behavior may imply greater relative stability for CpIr(CO) than for $Os(CO)_4$.[19] Nevertheless, despite the thermal stability of $Cp_3Ir_3(CO)_3$, reactions analogous to the extensive chemistry developed by direct substitution of $Os_3(CO)_{12}$[20] will not likely be accessible directly from $Cp_3Ir_3(CO)_3$. Alternative means of developing Cp_3Ir_3 chemistry are being investigated.

Acknowledgment. This research was supported at the University of Illinois by grants from the National Science Foundation (CHE 78-17911, 81-00140, and DMR 77-23999, 80-20250).

Registry No. $Cp_3Ir_3(CO)_3$, 80630-37-1; $CpIr(CO)H_2$, 78829-47-7; $CpIr(CO)_2$, 12192-96-0; $CpIr(CO)(PPh_3)$, 32612-68-3; $CpIr(CO)(PPhMe_2)$, 80630-38-2; CpIr(CO)(*t*-BuNC), 80630-39-3; $Cp_2Ir_2(CO)_3$, 80630-40-6; $CpIr(CO)Br_2$, 64867-78-3.

Supplementary Material Available: A listing of positional and thermal parameters for C_s-$Cp_3Ir_3(CO)_3$ (1 page). Ordering information is given on any current masthead page.

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(11) A similar structural feature is apparent for C_s-$Cp_3Rh_3(CO)_3$, except that the $Cp_2Rh_2(CO)_2$ moiety is doubly carbonyl bridged.[2c] For theoretical analysis of related compounds see: Hofmann, P.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. For the addition of unsaturated metal fragments to $(\eta^5\text{-}C_5Me_5)_2M_2(CO)_2$ (M = Co, Rh) see: Cirjak, L. M.; Huang, J.-S.; Zhu, Z.-H.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6673. Boag, N. M.; Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1171.

(12) A similar solvent effect was noted for the elimination of H_2 from $H_2Co[P(OMe)_3]_4^+$: Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978.

(13) Graham, W. A. G.; Oliver, A. J. *Inorg. Chem.* **1970**, *9*, 2653.

(14) $CpIr(CO)(PPhMe_2)$: IR (CH_2Cl_2) ν_{CO} 1915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.5 (m, 5 H), 5.16 (s, 5 H), 1.96 (d, 6 H, J = 10.5 Hz). CpIr(CO)(CN-*t*-Bu): IR (CH_2Cl_2) ν_{CO} 1939 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (s, 5 H), 1.30 (s, 9 H).

(15) Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2658.

(16) Treatment of $CpIr(CO)_2$ with $Me_3NO{\cdot}2H_2O$ also appears to generate CpIr(CO); but in this case, $Cp_2Ir_2(CO)_3$ is the major product: ^1H NMR ($CDCl_3$, 30 °C) δ 5.57 (s); ^{13}C NMR (CH_2Cl_2, −50 °C) 206 (s, 1 C), 172 (s, 2 C); IR (C_6H_{12}) ν_{CO} 1966, 1796 cm^{-1}; mass spectra m/e 600 (M^+) 572 (M − CO), 544 (M − 2CO), 516 (M − 3CO). $Cp_2Ir_2(CO)_3$ appears to be isostructural with $Cp_2Rh_2(CO)_3$: Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *10*, 337.

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(19) Whether the ease of H_2 loss from $CpIr(CO)H_2$ is due to more electron density at the metal center is not clear. $CpIr(PPh_3)H_2$ reacts with D_2 and CO more rapidly than does $CpIr(CO)H_2$. However, under similar conditions $(\eta^5\text{-}C_5Me_5)Ir(CO)H_2$ is much less reactive (Dimas, P.; Shapley, J. R., unpublished results).

(20) See especially the work of Deeming and co-workers reviewed by: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

Kinetics of Carbon Monoxide Activation: Reactions of Methoxide and of Hydroxide with Ruthenium and Iron Carbonyls[1]

Sir:

Nucleophilic activation of coordinated CO is a key feature of proposed mechanisms for homogeneously catalyzed processes such as the water-gas shift reaction[2] (WGSR) and the

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(1) Reported in part at the Symposium on Catalytic Activation of Carbon Monoxide, Second Chemical Conference of the North American Continent (180th National Meeting of the American Chemical Society), Las Vegas, NV, Aug 1980.

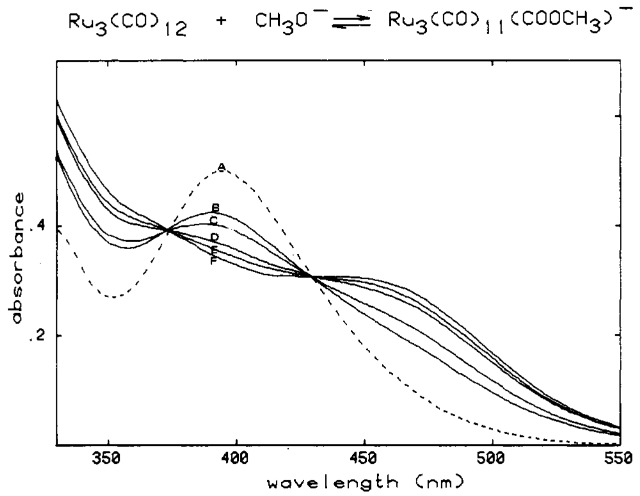

Figure 1. Electronic spectra of $Ru_3(CO)_{12}$ (7.3×10^{-5} M) in anhydrous methanol containing the following concentrations of added $NaOCH_3$: A, none; B, 7.4×10^{-4} M; C, 1.45×10^{-3} M; D, 5.2×10^{-3} M; E, 0.11 M; F, 0.22 M.

CO/H_2O or CO/H_2 reductions or reductive carbonylations of organic substrates.[2d,3] Particularly interesting catalysts for such reactions have been carbonyls of the iron triad $M_x(CO)_y$ (M = Fe, Ru, or Os). However, despite extensive mechanistic speculation concerning the activation of these by oxygen nucleophiles, very few quantitative kinetics data are currently available. To address this deficiency, we have initiated kinetic studies of the formation of methoxy- and hydroxycarbonyls according to eq 1. These reactions are quite fast for the

$$M_x(CO)_y + OR^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_x(CO)_{y-1}(CO_2R)^- \qquad (1)$$

$$R = H \text{ or } CH_3$$

substrates $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Ru(CO)_5$ each of which is dramatically more reactive than $Fe(CO)_5$.[4] These results provide a plausible explanation of the remarkable differences between the reported WGSR catalytic activities of iron and ruthenium carbonyls under conditions where mononuclear species are predominant.

Addition of $NaOCH_3$ to $Ru_3(CO)_{12}$ in methanol under CO (1 atm) leads to the spectral changes illustrated in Figure 1. Isosbestic points at 426 and 374 nm are maintained and a limiting spectrum is obtained at high $[CH_3O^-]$ consistent with the formation of a stable adduct I. Addition of excess

$$Ru_3(CO)_{12} + CH_3O^- \rightleftharpoons \underset{\text{I}}{Ru_3(CO)_{11}(CO_2CH_3)^-} \qquad (2)$$

CF_3COOH regenerates $Ru_3(CO)_{12}$ quantitatively. The adduct is also formed in THF solutions in which its IR spectrum displayed ν_{CO} bands at 2069 w, 2015 s, 1997 s, 1963 m, and 1595 w cm^{-1}, the last band attributed to the methoxycarbonyl function $-CO_2CH_3$. However, in the latter solvent, addition of excess CH_3O^- and/or replacement of the CO atmosphere by flushing with argon results in subsequent reactions of I to form new clusters not seen in CH_3OH solutions.[5] In contrast, addition of $NaOCH_3$ to $Ru(CO)_5$[6] in THF gives a stable product (isolable as the triphenylphosphine triphenylphosphoranylidenimidium salt) with an IR spectrum (2019 w, 1928 m, 1910 s, and 1625 w cm^{-1} in THF) consistent with the formation of the $Ru(CO)_4(CO_2CH_3)^-$ adduct.

Table I. Kinetics Data of Methoxycarbonyl and/or Hydroxycarbonyl Adduct Formation[a]

	solvent	k_1, L mol^{-1} s^{-1}	k_{-1}, s^{-1}
$Ru_3(CO)_{12}$			
+ OH^-	12.5% aq THF	1.2×10^4	~6
+ OCH_3^-	CH_3OH	2.0×10^3	3
	95% CH_3OH/THF	2.2×10^3	1.1
	10% aq CH_3OH[b]	1.8×10^3	3.5
$Ru(CO)_5$			
+ OH^-	12.5% aq THF	3.0×10^4	~10
+ OCH_3^-	CH_3OH	8.2×10^3	3
$Fe_3(CO)_{12}$			
+ OCH_3^-	CH_3OH	1.0×10^4	8
	10% aq CH_3OH[b]	7.2×10^3	3.5
$Fe(CO)_5$[c]			
+ OH^-	30% aq CH_3OH	70	
+ OCH_3^-	CH_3OH	1.5	1.3×10^{-2}

[a] At 25 °C; mixed-solvent ratios based on volume to volume preperations. [b] Total rates for formation of both hydroxy and methoxy adducts in this mixed solvent where the $[OH^-]/[CH_3O^-]$ ratio is ~0.03. [c] Data from ref 4.

Reaction of excess $NaOCH_3$ with $Fe_3(CO)_{12}$ in CH_3OH (under CO) follows a somewhat different pattern. An initial cluster methoxide adduct is rapidly formed, but this reacts further to give the mononuclear product[7] $Fe(CO)_4(CO_2CH_3)^-$ (see eq 3 and 4). Notably, the difference in the $M_3(CO)_{12}$

$$Fe_3(CO)_{12} + CH_3O^- \rightleftharpoons Fe_3(CO)_{11}(CO_2CH_3)^- \qquad (3)$$

$$Fe_3(CO)_{11}(CO_2CH_3)^- + 3CO + 2CH_3O^- \rightarrow 3Fe(CO)_4(CO_2CH_3)^- \qquad (4)$$

plus CH_3O^- reaction patterns is the likely cause of the disparate product distributions recently reported for the CO/H_2 reductive carbonylations of nitro aromatics when $Ru_3(CO)_{12}$ or $Fe_3(CO)_{12}$ is used with methoxide as a cocatalyst.[3d]

The initial adduct formed upon reaction of $Ru_3(CO)_{12}$ with NaOH in aqueous THF under CO has an electronic spectrum similar to that seen for I (Figure 1); however this species undergoes a slower subsequent reaction to give the hydride[8] $HRu_3(CO)_{11}^-$ (eq 5). Similarly, addition of NaOH (in aqueous THF) to $Ru(CO)_5$ leads to a product which has spectral properties analogous to those of the methoxide adduct but which reacts subsequently (more slowly) to give $HRu(CO)_4^-$ (eq 6).[9]

$$Ru_3(CO)_{12} + OH^- \rightleftharpoons Ru_3(CO)_{11}(CO_2H)^- \rightarrow HRu_3(CO)_{11}^- + CO_2 \qquad (5)$$

$$Ru(CO)_5 + OH^- \rightleftharpoons Ru(CO)_4(CO_2H)^- \rightarrow HRu(CO)_4^- + CO_2 \qquad (6)$$

Kinetics of initial adduct formation[10] (eq 1) were studied by stopped-flow techniques and are consistent with the rate

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(2) (a) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31–7. (b) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252–3. (c) Cheng, C. H.; Henrickson, D. E.; Eisenberg, R. *Ibid.* **1977**, *99*, 2791–2. (d) Kang, H.; Mauldin, C. H.; Cole, T.; Slegier, W.; Cann, K.; Pettit, R. *Ibid.* **1977**, *99*, 8323–5. (e) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D. *Ibid.* **1978**, *100*, 2925–7. (f) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *Ibid.* **1980**, *102*, 4688–94.

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(4) Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.

(5) Similar reactions subsequent to nucleophilic attack on a CO of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ in THF solution have been recently reported by: Kaesz, H. Paper 187 of the Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, Oct 1981.

(6) Synthesized from $Na_2Ru(CO)_4$ plus CO_2 in THF solution according to procedures analogous to those reported by: Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604–6.

(7) McLean, J. L. Ph.D. Dissertation, City University of New York, 1974.

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(10) The kinetics of the various subsequent reactions noted here are currently under study and will be reported elsewhere.

law expressed in eq 7. The k_1/k_{-1} ratios are equivalent to

$$-d[M_x(CO)_y]/dt = (k_1[OR^-] + k_{-1})[M_x(CO)_y] \quad (7)$$

the equilibrium constants for adduct formation determined from spectral changes as seen in Figure 1. The relevant rate data are summarized in Table I along with similar data obtained earlier[4] for $Fe(CO)_5$.

The three substrates $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Ru(CO)_5$ are all remarkably reactive toward each of the oxygen nucleophiles (OH^- being the more reactive) especially in comparison to $Fe(CO)_5$.[11] Given that adduct formation is faster for $Ru(CO)_5$ than for $Ru_3(CO)_{12}$, the cluster apparently provides no special advantage over the monomer in accomodating the developing negative charge in the reaction transition state. Preliminary kinetics studies in this laboratory on the reactions of osmium carbonyls with methoxide confirm this with $Os(CO)_5$ being considerably more reactive than $Os_3(CO)_{12}$. Furthermore under comparable conditions, the mononuclear complexes follow the order $Os(CO)_5 > Ru(CO)_5 >> Fe(CO)_5$ while the trinuclear complexes follow the order $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$. The failure of a cluster effect to be evidenced for the heavier metals accentuates the dramatic reversal of form for the iron carbonyls. One possible rationale for the surprising high reactivity of the triiron complex is that the presence of the bridging carbonyls (which are a structural feature of $Fe_3(CO)_{12}$[12] but not of $Ru_3(CO)_{12}$) raises the reactivity of this species from that of $Fe(CO)_5$ to give rates fortuitously comparable to the ruthenium species.

The observation that $Ru(CO)_5$ is orders of magnitude more reactive than $Fe(CO)_5$ toward the formation of hydroxycarbonyl adducts provides an important clue in explaining a startling observation regarding homogeneous catalysis of the water-gas shift reaction. Under high CO pressures (>25 atm) and at 125 °C, very low concentrations of ruthenium carbonyl ($<10^{-4}$ M) aqueous trimethylamine solutions are reported to display extraordinarily high catalytic activities for H_2 production via the WGSR.[13] Under these conditions the ruthenium species are proposed to be largely mononuclear. Under similar conditions, catalysts prepared from $Fe(CO)_5$ in aqueous trimethylamine solutions are nearly 4 orders of magnitude less active.[2d] Mechanistic studies of the WGSR catalysis by $Fe(CO)_5$ in alkaline alcohol solutions have identified the reaction of base with $Fe(CO)_5$ as the rate-limiting step of the catalysis cycle.[4,14] In the context of this mechanism, the much greater susceptibility of $Ru(CO)_5$ to hydroxide attack would explain the extraordinary activity of the mononuclear ruthenium catalyst.

In summary, these studies provide important insight in interpreting the roles of nucleophilic activation in the metal carbonyl catalysis of two different reactions[2,3d] involving carbon monoxide as a reductant. Continuing studies are directed toward further evaluation of the roles played by mononuclear and polynuclear metal centers in activating CO toward various nucleophiles and toward a more complete elucidation of the reaction mechanisms of these and subsequent reactions.

Acknowledgment. This research was sponsored by the U.S. Department of Energy-Office of Basic Energy Sciences. Ruthenium used is these studies was provided on loan by Johnson-Matthey Inc. Dr. Haim Cohen, formerly of these laboratories, carried out preliminary rate measurements of the $Ru_3(CO)_{12}$ system.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_5$, 16406-48-7; $Fe_3(CO)_{12}$, 17685-52-8; OH^-, 14280-30-9; OCH_3, 2143-68-2.

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(11) The rates of $Fe(CO)_5$ plus CH_3O^- reactions have been qualitatively confirmed by independent studies in this laboratory. Notably all these systems including $Fe(CO)_5$ are many orders of magnitude more reactive with OH^- than is free CO, which reacts slowly with aqueous base at elevated temperatures (Iwata, M. *Chem. Abstr.* **1969**, *70*, 6989*v*).

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Stepwise Formation of Triosmium Edge Double-Bridged μ-H,μ-O=C(Nu) Decacarbonyl Complexes, Nu = NRR', OR, or R. Reversal of Barrier Heights in the Fluxional Behavior of the Anions $[Ru_3(\mu\text{-}O{=}CNMe_2)(\mu\text{-}CO)_3(CO)_7]^-$ and $[Os_3(\mu\text{-}O{=}CNMe_2)(CO)_{10}]^-$

Sir:

We wish to report studies on the reaction of nucleophiles with $Os_3(CO)_{12}$ (**1**)[1] and $Ru_3(CO)_{12}$[1a,2] at room temperature and below, which we believe play an important role in the transformations of carbon monoxide at these polynuclear metal centers.[3] The system studied initially is that using primary or secondary amines with **1**. Our observations and the experimental conditions employed are summarized in Scheme I. The ionic intermediates shown in this scheme were identified through spectroscopic studies described as follows.

When **1** is treated at 0 °C with $LiNMe_2$, it is initially converted to a salt of the anion [**2a**]$^-$. When the solution warms to room temperature, carbon monoxide is evolved from [**2a**]$^-$, forming [**3a**]$^-$ quantitatively within about 1 h. Loss of the carbonyl group is accompanied by the transformation of the η^1-carboxamido ligand into the μ form.

Spectroscopic data in accord with these structural assignments were determined for the $[PPN]^+$ salts[4] of [**2a**]$^-$ and [**3a**]$^-$. In [PPN][**2a**] a strong IR absorption is seen at 1549 cm^{-1} (THF solution),[5] which may be attributed to the ν(C=O) absorption of the η^1-$C(O)NMe_2$ group. Coordination of the oxygen atom to the metal center causes this absorption to shift to 1503 cm^{-1} in [PPN][**3a**] (CH_2Cl_2 solution).[6] The ^1H NMR spectrum of [PPN][**2a**] shows a singlet for the dimethylamino group that is temperature dependent (δ (THF-d_8) 3.36 at −40 °C and 2.62 at 35 °C). The spectrum of [PPN][**3a**] shows two separate singlets that are temperature independent (δ (THF-d_8) 3.08, 2.69). Coordination of the acyl oxygen and restricted rotation at the C–NMe_2 bond are re-

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(4) (a) [PPN][Cl] = bis(triphenylphosphine)iminium chloride; Alfa Division, Ventron, Danvers, MA 01923. The Chemical Abstracts recommended name for $[PPN]^+$ is bis(triphenylphosphoranediyl)nitrogen(1+). (b) A solution of the $[PPN]^+$ salt is prepared by adding an equivalent amount of $NaOCH_3/HOCH_3$ at 0 °C to a solution of **1** in $HNMe_2$/THF (1:3) followed by adding a slight excess of [PPN][Cl]. The solvent is removed, the residue is redissolved at 0 °C in THF, and the resulting solution is filtered.

(5) Carbonyl absorptions for [PPN][**2a**] (cm^{-1}): 2087 w, 2026 s, 2008 m, 1993 vs, 1959 m.

(6) Carbonyl absorptions for [PPN][**3a**] (there is a systematic shift of the carbonyl absorptions to lower energy) (cm^{-1}): 2063 w, 2006 s, 1990 s, 1971, 1937 m, 1925 m.

0020-1669/82/1321-1704$01.25/0