

Facile Acyl/Carbonyl Scrambling in the Anionic Acyl Complex $[\text{Cr}(\text{CO})_5\{\text{C}(\text{=O})\text{Ph}\}]^-$

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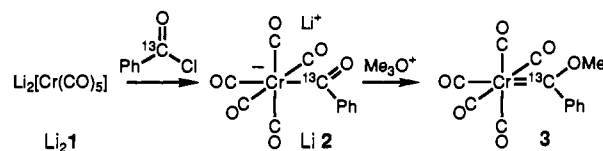
Anionic acyl complexes $[\text{Cr}(\text{CO})_5\{\text{C}(\text{=O})\text{R}\}]^-$ are the key intermediates in the classical Fischer route to Cr carbene complexes $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OR})\text{R}\}]^1$ and in Semmelhack's more recent approach² which involves addition of an acyl halide to $[\text{Cr}(\text{CO})_5]^{2-}$ (1^{2-}) followed by acyl alkylation. The latter offers an obvious approach to the synthesis of carbene complexes labeled on the carbenoid carbon, and we recently attempted such a sequence using $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$. We now wish to report that although this approach *can* be used to prepare labeled $[\text{Cr}(\text{CO})_5\{\text{C}(\text{=O})\text{Ph}\}]^-$ (**2**) and $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OMe})\text{Ph}\}]$ (**3**) (Scheme I), intermolecular thermal scrambling between the $\text{C}=\text{O}$ ligands and the acyl group in **2** is surprisingly facile.

Addition of 0.95 equiv of $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$ to a stirred solution of $\text{Li}_2\text{-1}$ in THF³ at -78°C resulted in rapid formation of the lithium acylate Li-2 ,⁴ and reaction was complete in a few minutes at -78°C (color change and IR). The solvent was removed at low temperature, the solid was suspended in H_2O , and 1.4 equiv of $[\text{Me}_3\text{O}]\text{BF}_4$ were added to give **3** (61%) labeled primarily at the carbenoid carbon as indicated by a strong ^{13}C NMR resonance at δ 351.0 and weak *trans* and *cis* carbonyl resonances at δ 224.1 and 216.1 consistent with natural abundance ^{13}C levels.

The isotopic composition of the labeled **3** was determined by MS.^{5,6} The isotopic envelope of the $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]^+$ (4^+) fragment⁷ indicated that 94.4% of the ions had been enriched by one (and only one) ^{13}C atom relative to the 4^+ cluster of an unlabeled sample of **3**, and the envelope of the $[\text{Cr}\{\text{C}(\text{OMe})\text{Ph}\}]^+$ (5^+) ion indicated that 93.5% of 5^+ ions are mono ^{13}C enriched. This implies that the carbenoid carbon accounts for 99% of the enrichment and that Scheme I can indeed be used to prepare carbene complexes labeled at the carbenoid carbon.

The isotopic analysis of labeled **3** incidentally indicated that it contained ca. 13% ^{18}O per ^{13}C . This ^{18}O is an isotopic impurity in commercial " $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$ ", and the MS of $\text{PhC}(\text{O})\text{NHPH}$

Scheme I



prepared from aniline and this $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$ established that the acyl group was 99.3 atom % ^{13}C and 12.7 atom % ^{18}O .

When a ^{13}C -labeled solution of Li-2 was allowed to warm to room temperature before solvent removal and alkylation, we were surprised to find (^{13}C NMR) ^{13}C enrichment of the carbonyl ligands in **3** comparable to that observed for the carbenoid carbon. Isotopic analysis of the 4^+ and 5^+ envelopes in mass spectra of this sample of **3** established that the carbenoid carbon was 17 ± 1 atom % ^{13}C while the carbonyl carbons were 14 ± 1 atom % ^{13}C .

The fortuitous presence of ^{18}O in the starting $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$ allowed us to establish that the acyl C and O remained coupled throughout this scrambling reaction. The isotopic envelope of the 5^+ ion established that 12.3% of the 5^+ ions which contain ^{13}C also contain ^{18}O . This is indistinguishable from the 12.7% predicted if the C and O remain coupled and much higher than the 2.2% ^{18}O per ^{13}C carbene ligand predicted if C and O scrambling is extensive and independent, such that the ^{18}O becomes randomly distributed between the carbene and carbonyl ligands. These data rule out an oxide-transfer scrambling mechanism related to the oxide transfer from coordinated CO_2 to coordinated CO which we have observed in anionic CO_2 complexes.^{5b,8}

The presence of several carbonyl sites in 4^+ ions is also mechanistically revealing—intramolecular scrambling cannot lead to more than one ^{13}C per molecule, but there are up to four ^{13}C atoms in 4^+ ions. Scrambling must therefore include *intermolecular* exchange of ^{13}C , presumably as carbon monoxide since we also know that ^{18}O remains coupled to its adjacent ^{13}C . It would appear that intermolecular $\text{C}=\text{O}$ exchange is at least as fast as exchange between the acyl group and the $\text{C}=\text{O}$ ligands, since there is good agreement between the numbers of ^{13}C atoms per molecule observed experimentally in 4^+ ions and the numbers calculated on the assumptions of 17.3 atom % ^{13}C in the carbenoid site, 14.1 atom % ^{13}C in the carbonyls, and a random intermolecular distribution of the labeled $\text{C}=\text{O}$.⁹

It seemed probable that scrambling occurred in Li-2 and was not a side reaction consequential upon alkylation. This was confirmed by ^{13}C NMR observation as a sealed sample of labeled Li-2 in THF, prepared at -196°C , was warmed. When NMR observation began at -60°C , the only enriched site was that assigned to the benzoyl carbon at δ 311.8, and no ^{13}C changes were observed until the temperature reached ca. 15°C . Scrambling under these conditions was not as rapid as in the mass spectral experiments but was extensive after several days at room temperature.

Our ^{13}C NMR and MS experiments suggest the scrambling mechanism in Scheme II, in which loss of a *cis* $\text{C}=\text{O}$ allows rapid and reversible CO elimination from the acyl to form $[\text{Cr}(\text{CO})_5\text{Ph}]^-$ (**6**).¹⁰ Scheme II should allow exchange with external CO at the same rate as acyl/CO scrambling, and we have confirmed this

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(9) Number of ^{13}C atoms in 4^+ ions (experimentally observed percentage, calculated percentage): 0 (44.8, 45.0); 1 (39.5, 39.0); 2 (13.7, 13.8); 3 (1.9, 2.3); 4 (0.3, 0.2).

(10) Interconversion of **2** and **6** could involve coordinatively unsaturated intermediates generated by loss of a *cis* $\text{C}=\text{O}$ from **2**, and/or similar acyls with a *cis* solvent molecule, but we have no evidence which requires us to postulate the existence of such intermediates. The kinetic studies which would be required to obtain further evidence on this point are probably impractical in this reactive system.

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(2) Semmelhack, M. F.; Lee, G. R. *Organometallics* 1987, 6, 1839.

(3) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* 1985, 4, 1354.

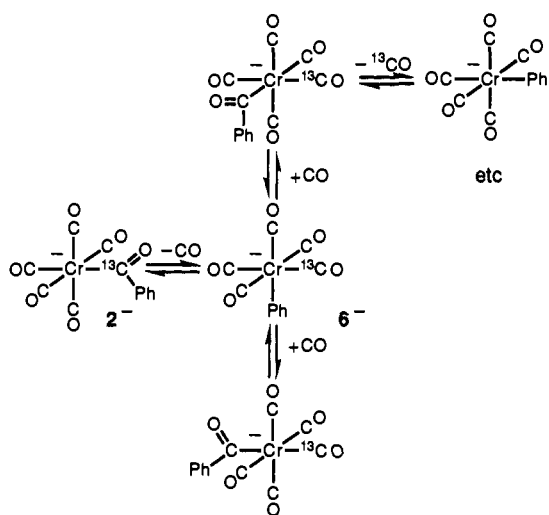
(4) $[\text{NMe}_2]\text{-2}$ has been previously characterized.^{1b} The spectroscopic characteristics of Li-2 include IR ($\nu_{\text{C}=\text{O}}$, THF) 2040 (w), 1906 (vs, br); ^{13}C { ^1H } NMR (acetone- d_6 , 75.45 MHz) δ 305.8 (s, C(O)Ph), 227.3 (s, *trans* CO), 222.1 (s, *cis* CO), 156.7 (s, Ph, *i*-C), 127.6 (s, Ph, *p*-C), 127.3 (s, Ph, *m*(*o*)-C), 123.6 (s, Ph, *o*(*m*)-C).

(5) (a) Biemann, K. *Mass Spectrometry, Organic Chemical Applications*; McGraw Hill: New York, 1962; Chapter 5. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* 1982, 104, 6797.

(6) Mass spectrum of unlabeled **3** (EI, 15 eV, only the ^{52}Cr peaks of clusters exhibiting the Cr isotope pattern are listed; this includes all major clusters with $m/z > 120$). Data are given as follows: m/z (relative intensity, assignment) 312 (4, $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 284 (22, $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 256 (51, $[\text{Cr}(\text{CO})_3\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 228 (32, $[\text{Cr}(\text{CO})_2\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 200 (72, $[\text{Cr}(\text{CO})\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 172 (100, $[\text{Cr}\{\text{C}(\text{OMe})\text{Ph}\}]^+$), 136 (24, $[\text{Cr}(\text{CO})_3]^+$).

(7) This is the fragmentation ion which is most suitable for isotopic characterization of the carbonyl ligands: as a polycarbonyl ion its isotopic envelope contains information about intermolecular exchange processes; there are few background ions in this region; and this ion is much more intense than the molecular ion, which at 4% of the parent ion⁶ is too weak for quantitative isotopic analysis.

Scheme II



by preparing Li-2 from unlabeled PhC(O)Cl under ca. 1 atm of ^{13}C O and allowing the Li-2 to warm to room temperature before alkylation. This gave 3 which was 9 ± 1 atom % ^{13}C in the carbonyl and the carbene ligands, as determined from the isotopic envelopes of 4^+ and 5^+ fragmentation ions. The suggestion that CO dissociation from Li-2 is at least as rapid as CO elimination from the acyl ligand is also supported by our NMR study—exchange of $^{13}\text{C}=\text{O}$ from Li2 into $[\text{Cr}_2(\text{CO})_{10}]^{2-}$, present as an initial byproduct of addition of $\text{Ph}^{13}\text{C}(\text{O})\text{Cl}$ to Li₂, occurs at a rate indistinguishable from enrichment of the *cis* and *trans* C=O ligands in Li₂.¹¹

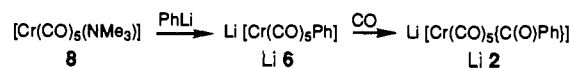
If Scheme II is to account for our observations, C=O addition to Li6 must be more rapid than that to isologous $[\text{W}(\text{CO})_5\text{Ph}]^-$ (7-) (7 days).¹² A route analogous to that used to prepare 7-¹² did not provide access to 6-, but addition of PhLi to $[\text{Cr}(\text{CO})_5(\text{NMe}_3)]$ (8)³ (Scheme III) gives Li-6¹³ immediately at room temperature (IR). Addition of ca. 1 atm of CO generates Li-2 (isolated as $[\text{NEt}_4]\text{-2}$ in 69% yield¹⁴) under mild conditions (<1 h at room temperature) consistent with the intermediacy of Li-6

(11) This reaction accounts for the observation of total ^{13}C levels in scrambled 3 lower than the 0.993 ^{13}C per molecule of added PhC(O)Cl .

(12) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

(13) Counterion exchange with $[\text{NEt}_4]\text{Br}$ gave $[\text{NEt}_4]\text{-6}$ contaminated with $[\text{NEt}_4]\text{Br}$. Separation of the salts was not feasible, but ^1H NMR indicated a 64% yield of $[\text{NEt}_4]\text{-6}$: IR ($\nu_{\text{C}=\text{O}}$, THF) 2026 (w), 1893 (vs), 1853 (m); $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , 75.45 MHz) δ 228.9 (s, *trans*-CO), 225.0 (s, *cis*-CO), 172.1 (s, Ph, *i*-C), 145.6 (s, Ph, *o(m)*-C), 125.9 (s, Ph, *m(o)*-C), 121.1 (s, Ph, *p*-C).

Scheme III



in the scrambling reaction. In situ alkylation of Li-2 gave 3 in 49% yield from 8—this establishes Scheme III as a viable alternative to the Fischer and Semmelhack syntheses of 3.

The speed of the scrambling reaction within 2- is surprising and requires that the rate of CO dissociation from 2- be faster than the established rate of CO dissociation from 3.¹⁵ This may indicate that coordination of the acyl oxygen to Cr provides intramolecular assistance for the dissociation in a manner analogous to that proposed to account for rapid *cis* CO exchange with anionic carboxylate complexes $[\text{M}(\text{CO})_5\{\text{OC}(\text{O})\text{R}\}]$.¹⁶

Rapid scrambling within 2- also implies facile C=O elimination from the acyl ligand, consistent with the alkyl migration model for CO elimination from acyls.¹⁷ The carbanion character of the aryl in 2- should accelerate a nucleophilic migration, and, together with the observation of rapid C=O insertion in anionic iron alkyls $[\text{Fe}(\text{CO})_4\text{R}]^-$,¹⁸ our results suggest that facile acyl/C=O scrambling may be more common in anionic acyl complexes than in neutral acyl complexes. The mild conditions under which the reaction occurs and the ability to control it thermally should render the scrambling sequence a useful tool in mechanistic studies of the synthetically unique reactions of Cr carbene complexes, particularly those which involve carbene/carbonyl coupling.¹⁹

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(14) This yield is corrected for the presence (^1H NMR) of some $[\text{NEt}_4]\text{Br}$.
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