

## Acyloxy-carbene Complexes and Their Reaction with Hydrogen Azide

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**Summary** The new class of compounds  $R \cdot C(X) \cdot OAc$  [ $R = 2\text{-furyl}$  or  $CH_3SiMe_3$ ;  $X = Cr(CO)_5$ ] react with  $HN_3$  to give nitriles and isonitriles.

REACTION of an acyl halide,  $R^1COCl$ , with a lithium acyl-carbonyl metallate,  $Li[R^2CO \cdot M(CO)_n]$ , produces either unsymmetrical ketones,  $R^2R^1CO$  ( $M = Fe$ ;  $n = 4$ ) or ene-diol diesters,  $(R^2 \cdot C \cdot OCOR^1)_2$  ( $M = Ni$ ;  $n = 3$ ).<sup>1</sup> We report the isolation of the intermediate acyloxy-carbene complex,  $R^1CO \cdot O \cdot C(R^2) \cdot M(CO)_n$  ( $M = Cr$ ;  $n = 5$ ) which offers an increased range of synthetic application.<sup>2</sup>

- $LCr(CO)_5$
- (1)  $L = C(Fu)O \cdot COMe$   
 (2)  $L = C(Fu)N_3$   
 (3)  $L = NCFu$   
 $Fu = 2\text{-Furyl}$

Acetyl chloride reacts with  $Me_4N[(Fu) \cdot CO \cdot Cr(CO)_5]$  ( $Fu = 2\text{-furyl}$ ) in methylene chloride solution in the dark at room temperature to give the complex, (1), recrystallised from hexane as air- and light-sensitive purple-red needles, m.p.  $71^\circ$ . (1) reacts with nucleophiles  $R_n^3XH$  ( $X = O, N, S$ ;  $R^3 = \text{alkyl, aryl, acyl, H}$ ) in the normal manner.<sup>3</sup>

In benzene-hexane solution (1:50) in the dark, (1) reacts with  $HN_3$  to give a red solution of the azido-carbene complex, (2), which is very sensitive to both heat and light. On concentration at room temperature, the red solution of (2) becomes pale yellow and yields (3), m.p.  $108^\circ$ ;  $\nu_{max}$   $2234$  ( $CS_2$ )  $cm^{-1}$ ;  $\delta$  [ $(CD_3)_2CO$ ]  $-674$  (1H, dd, 4-H),  $-758$  (1H, dd, 3-H), and  $-795$  (1H, dd, 5-H) Hz. Comparison of these results with data for 2-furanonitrile<sup>3</sup> and for other  $Cr(CO)_5\text{-NCR}$  compounds,<sup>4</sup> shows that the contribution of the dipolar form of the ligand is considerably increased by complexing.<sup>5</sup>

Attempts to trap a hypothetical nitrene-type intermediate were unsuccessful and this, together with the mild conditions under which (3) is formed from (2) suggests that a metal-promoted concerted process is operating.<sup>6</sup>

The salt  $\text{Me}_4\text{N}[\text{Me}_3\text{SiCH}_2\text{CO}\cdot\text{Cr}(\text{CO})_5]$ , m.p. 94°;  $\delta$   $[(\text{CD}_3)_2\text{CO}] - 275$  Hz ( $-\text{CH}_2-$ ), (4), reacts rapidly with acetyl chloride at room temperature; in  $\text{CH}_2\text{Cl}_2$  solution, the sole chromium-containing product was identified as  $\text{Me}_4\text{N}[\text{Cr}(\text{CO})_5\text{Cl}]$  (97%).<sup>7</sup> In acetonitrile solution the corresponding product is  $\text{MeCN}\cdot\text{Cr}(\text{CO})_5$ ,<sup>4</sup> (5). Spectroscopic measurements of the alkoxy-compound  $(\text{CO})_5\text{Cr C}(\text{OEt})\text{CH}_2\text{SiMe}_3$ , m.p. 1° [ $\delta$  ( $\text{CCl}_4$ )  $-358$  Hz ( $-\text{CH}_2-$ ) ( $\text{CCl}_4$ )], (6), suggest an analogy between the  $\text{Me}_3\text{SiCH}_2$ -group and the 2-N-methyl pyrrol group<sup>8</sup> in terms of conjugative electron releasing properties. The addition of ethanol to (6) causes Si- $\text{CH}_2$  cleavage<sup>8</sup> at room temperature to give the known<sup>9</sup>  $(\text{CO})_5\text{Cr}$

$\text{C}(\text{OEt})\text{Me}$ , while with ammonia, (6) undergoes cleavage and substitution to give the known<sup>10</sup>  $(\text{CO})_5\text{Cr C}(\text{NH}_2)\text{Me}$ .

Addition of  $\text{HN}_3$  in benzene to a mixture of (4) and acetyl chloride (1:1) in methylene chloride at 0 °C, followed by slow warming to room temperature produces both  $(\text{CO})_5\text{CrCNMe}$ , m.p. 69°, (7), (major product) and (5) (minor product). The former is analogous to the product expected from a Schmidt-type rearrangement. Whether Si- $\text{CH}_2$  cleavage occurs before or after rearrangement is unclear and further studies of this reaction, which appears to involve concerted migration of both metal and alkyl groups from carbon to nitrogen to give (5) and (7) respectively, are in hand.

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