Acknowledgment. We thank Philip C. Bevilacqua for suggesting the purine substitution and for stimulating discussions and Adam E. Peritz for synthesizing blocked adenosine for oligonucleotide synthesis. This work was supported by National Institutes of Health Grant GM22939. J.S.L. is an E. H. Hooker Fellow.

Registry No. 1, 133324-30-8; **2** (isomer 1), 133324-31-9; **2** (isomer 2), 133324-59-1; **3** (isomer 1), 133324-32-0; **3** (isomer 2), 133324-60-4; **4** (isomer 1), 133324-33-1; **4** (isomer 2), 133324-61-5; **5**, 70337-80-3; **6**, 133324-34-2; **7**, 133324-35-3; **8**, 133324-36-4; **9**, 133324-37-5; **10**, 133348-46-6; **11** (isomer 1), 133324-38-6; **11** (isomer 2), 133324-62-6; **12** (isomer 1), 133324-39-7; **12** (isomer 2), 133324-63-7; **13** (isomer 1), 133324-40-0; **13** (isomer 2), 133324-64-8; **14** (isomer 1), 133324-41-1; **14** (isomer 2), 133324-65-9; **15** (isomer 1), 133348-47-7; **15** (isomer 2), 133324-66-0; **16** (isomer 1), 133324-42-2; **16** (isomer 2), 133324-67-1; A, 73-24-5; G, 73-40-5; P, 120-73-0; I, 68-94-0; PTSA, 6192-52-5; TEAHF, 29585-72-6; DMTr-Cl, 40615-36-9; DMAP, 1122-58-3; TPS-Cl, 6553-96-4; DHP, 110-87-2; rGCGAGCG, 124154-71-8; rGCGPGCG, 133324-43-3; rGCIAGCG, 133324-44-4; rGCIPGCG, 133324-45-5; rGCPPGCG, 133324-46-6; rGCAAGCG, 129173-86-0; rGC2AGCG, 133348-48-8; rGCAGGCG, 129173-87-1; rGCPGGCG, 133324-47-7; rGCAIGCG, 133324-48-8; rGGCGAGCC, 129173-88-2; rGGCGPGCC, 133324-49-9; rCGCAAGCG, 121186-88-7; rCGCAGGCG, 129173-89-3; rCGCPGGCG, 133324-50-2; rCGCAIGCG, 133324-51-3; rGCGCGp, 101696-92-8; rGGCGCCP, 101696-96-2; rCGCGCGp, 99508-76-6; rAGCGCG, 133324-52-4; rPGCGCG, 133324-53-5; rAGCGCGA, 133324-54-6; rAGCGCGP, 133348-49-9; rPGCGCGP, 133324-55-7; rGAGCGCGA, 133324-56-8; rGPGCGCGP, 133324-57-9; rGCCGGAP, 101696-83-7; rGCCGGAG, 133324-58-0; rGCGC, 73942-16-2; rCCGG, 55048-62-9; 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane, 69304-37-6; isobutyric acid anhydride, 97-72-3; diisopropylethylamine, 7087-68-5; diisopropylammonium tetrazolide, 93183-36-9; bis(diisopropylamino)(β-cyanoethoxy)phosphine, 102691-36-1; 9-(2′-*o*-tetrahydropyranyl-5′-*o*-(dimethoxytrityl)-β-D-ribofuranosyl)hypoxanthine, 126647-53-8; hydrazine, 301-01-2; nebularine, 550-33-4; guanosine, 118-00-3.

Supplementary Material Available: One figure showing plots of T_M^{-1} vs log C_T for rAGCGCG, rAGCGCGA, rGGCGPGCC, rPGCGCG, rPGCGCGP, rAGCGCGP, and rGCCGGAG and one figure with circular dichroism spectra for rGCAAGCG, rGCPPGCG, rGC2AGCG, rGCCGGAG, rAGCGCGA, rAGCGCGP, and rPGCGCGP (2 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Observation of an Unprecedented Equilibrium between Alkyl–Carbonyl, η^2-Acyl, and Agostic Acyl Isomeric Structures†

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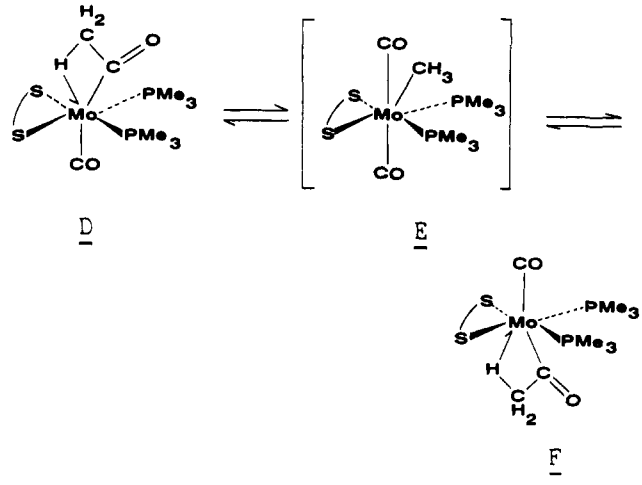
Bidentate acyl coordination is very commonly encountered among the early transition metals,[1] including the 6d metals.[2-5] Recent studies carried out in this[5] and other laboratories[6,7] have demonstrated the existence of fast equilibria between η^2-acyl complexes and their isomeric alkyl–carbonyl formulations (structures B and A, respectively). On the other hand, an earlier contribution[3b] from our group has provided an unprecedented acetyl, $Mo(\overline{C(O)CH_3})(S_2CNMe_2)(CO)(PMe_3)_2$ (**1**), in which there is a strong agostic interaction[8] between the metal center and one of the acetyl β-C–H bonds (structure C).

Scheme I



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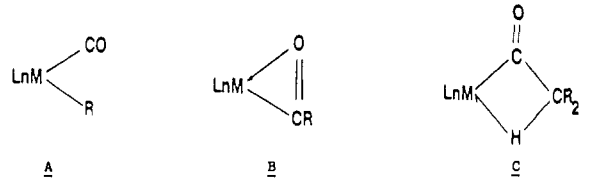

A B C

† Dedicated to Professor R. Usón on the occasion of his retirement.

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In an effort better to understand the factors that govern the adoption of this peculiar coordination mode of the acyl ligand and the relative thermodynamic and kinetic stabilities of the isomeric structures A–C, a systematic study of complexes of composition $Mo(C(O)CH_3)(S_2CX)(CO)(PMe_3)_2$ (X = NR_2, OR) has been undertaken. As discussed below, this has resulted in the first observation of a thermodynamic equilibrium among the three isomeric formulations A, B, and C.

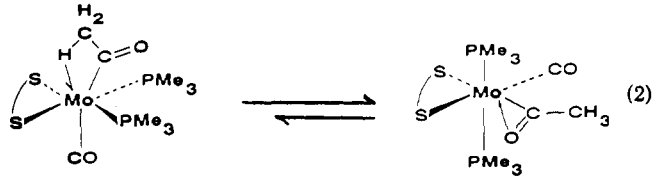
Compounds **2**–**5** have been prepared as shown in eq 1. Not unexpectedly, the dithiocarbamate derivatives **2** and **3** behave similarly to **1**, with the acetyl ligand involved in an agostic in-

$$Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3 + NaS_2CX \longrightarrow \overline{Mo(C(O)CH_3)}(S_2CX)(CO)(PMe_3)_2 + PMe_3 + NaCl \quad (1)$$

2, X = N-*i*-Pr_2
3, X = NC_5H_{10}
4, X = OMe
5, X = O-*i*-Pr

teraction with the molybdenum atom (i.e., structure C) both in solution and in the solid state.[9,10] An interesting feature of these compounds, which was not originally investigated for **1**, is the fluxionality they undergo in solution. For example, their $^{13}C\{^1H\}$ NMR spectra (20 °C, CD_2Cl_2) show only one triplet ($^2J_{CP}$ ca. 30 Hz) in the carbonyl region. Upon cooling, this signal broadens, eventually coalesces (−50 °C, data for **1**), and finally converts into two triplets at temperatures below −75 °C. The first, at 243.8 ppm ($^2J_{CP}$ = 30 Hz, data for **1**), is due to the metal-bound carbonyl ligand while the second is assigned to the agostic acetyl group (259.2 ppm, $^2J_{CP}$ = 30 Hz) on the basis of gated-decoupling experiments. It is clear that at room temperature a fast exchange between the two degenerate ground-state structures D and F is taking place, through the intermediacy of an alkyl–carbonyl species, tentatively formulated as in E (Scheme I).

The IR spectra of solid samples of the xanthate derivatives **4** and **5** exhibit two carbonyl absorptions at ca. 1790 (s) and 1615 (m) cm^{-1}, i.e., with frequencies very similar to those found for the related dithiocarbamates **1**–**3**. This is in accord with an agostic formulation, $\overline{Mo(C(O)CH_3)}(S_2COR)(CO)(PMe_3)_2$, for these complexes in the solid state. When crystals of **5** are dissolved and the resulting solution is cooled at −90 °C, a mixture of two species, agostic acyl **5C** and η^2-acyl **5B**, which can be readily identified by their characteristic NMR properties, is obtained[11] (eq 2).



(2)

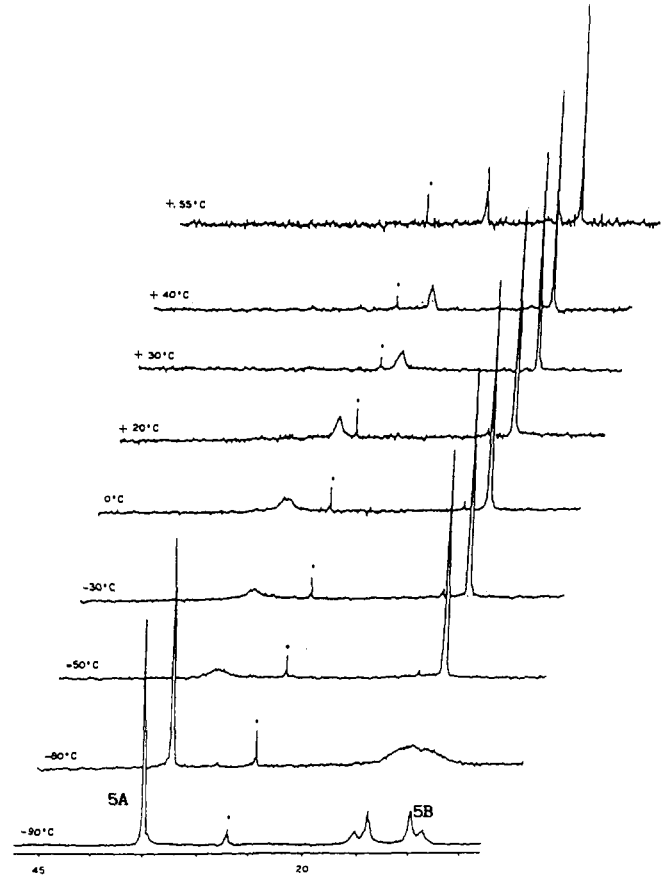


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (CD_3COCD_3) of the thermodynamic mixture of the three isomers of **5**. The dot denotes a minor impurity.

Upon warming at room temperature, the presence of a third species can be inferred. This is best shown by variable-temperature $^{31}P\{^1H\}$ NMR studies (Figure 1). Thus, two sets of resonances, a singlet at 35 ppm and an AB quartet centered at ca. 12 ppm, are observed in the spectrum of **5** recorded at −90 °C (CD_3COCD_3), corresponding to the agostic **5C** and η^2-acyl **5B** isomers, respectively.[12] The rocking motion[2b] of the η^2-acyl ligand in **5B** becomes fast at −50 °C and time-averages the environments of the PMe_3 ligands, which consequently give rise to a singlet that remains sharp in the temperature range studied (up to 55 °C). Parallel to these changes,[13] the resonance due to the agostic acetyl broadens and shifts dramatically to higher field until at 55 °C it becomes a sharp singlet centered at 19.2 ppm. Further heating of the sample is prevented by its thermal instability. Clearly, a third species whose concentration is strongly temperature dependent is in fast equilibrium with the agostic acetyl. We propose this to be the isomeric methyl–carbonyl complex $Mo(CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)_2(PMe_3)_2$ (**5A**) on the basis of the following observations: (i) The ^1H NMR resonance of the acetyl protons of **5C** shifts appreciably to high field upon raising the temperature (δ 1.81 ppm, −50 °C; 1.46 ppm, 20 °C; $C_6D_5CD_3$ solution), that is, to the region expected for a

(9) A single-crystal X-ray study of complex **3** has been carried out. Gutiérrez-Puebla, E.; Monge, A., personal communication.

(10) Selected spectroscopic data (20 °C) for **3** are as follows: IR (Nujol mull, cm^{-1}) 1789, 1608 (ν(CO)), 1503 (ν(CN)); IR (CH_2Cl_2 solution, cm^{-1}) 1789, 1605 (ν(CO)), 1492 (ν(CN)); ^1H NMR ($C_6D_5CD_3$, 200 MHz) δ 1.08 (br s, 6 H, CH_2), 1.42 (filled-in d, 18 H, $J_{HP_{app}}$ = 8.5 Hz, PMe_3), 1.91 (br s, 3 H, $C(O)CH_3$), 3.61 (br s, 4 H, CH_2); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$) δ 27.4 (s); $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$) δ 13.2 (br s, CH_3), 20.0 (d, $^1J_{CP}$ = 31.2 Hz, PMe_3), 28.8 (s, CH_2), 30.2 (s, CH_2), 52.6 (s, CH_2), 206.3 (t, $^3J_{CP}$ = 10.0 Hz, S_2C), 250.7 (t, $^2J_{CP}$ = 30.1 Hz, CO and $COCH_3$).

(11) Selected spectroscopic data (20 °C) for complex **5**: IR (Nujol mull, cm^{-1}) 1802, 1620 (ν(CO)); IR (THF solution, cm^{-1}) 1912, 1836, 1807, 1789, 1624, 1506 (ν(CO)). **5A** ⇌ **5C**: ^1H NMR ($C_6D_5CD_3$, 200 MHz) δ 1.16 (d, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), 1.37 (d, $J_{HP_{app}}$ = 8.5 Hz, PMe_3), 1.46 (t, J_{HP} = 3.0 Hz, $C(O)CH_3$), 5.50 (m, $CH(CH_3)_2$); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$) δ 23.3 (br s); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 0.6 (t, $^2J_{CP}$ = 5.8 Hz, $C(O)CH_3$), 15.0 (t, $J_{CP_{app}}$ = 14.0 Hz, PMe_3), 21.7 (s, $CH(CH_3)_2$), 77.2 (s, $CH(CH_3)_2$), 224.5 (t, $^3J_{CP}$ = 8.3 Hz, S_2C), 248.2 (t, $^2J_{CP}$ = 25.2 Hz, CO and $COCH_3$). **5B**: ^1H NMR ($C_6D_5CD_3$) δ 1.20 (d, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), 1.55 (t, $J_{HP_{app}}$ = 3.6 Hz, PMe_3), 2.50 (s, $C(O)CH_3$), 5.50 (m, $CH(CH_3)_2$); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$) δ 9.1 (s); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 16.1 (t, $J_{CP_{app}}$ = 11.8 Hz, PMe_3), 21.7 (s, $CH(CH_3)_2$), 22.3 (s, $C(O)CH_3$), 75.4 (s, $CH(CH_3)_2$), 223.0 (t, $^3J_{CP}$ = 6.1 Hz, S_2C), 237.6 (t, $^2J_{CP}$ = 14.1 Hz, CO), 280.3 (t, $^2J_{CP}$ = 16.0 Hz, $C(O)CH_3$).

(12) The agostic acyl **5C** is the only species existing in the solid state. Accordingly, when crystalline **5C** is dissolved at −60 °C in tetrahydrofuran, a solution of **5C** containing minor amounts of **5A** is obtained, while at room temperature an equilibrium among the three isomers **5A**, **5B**, and **5C** is quickly attained. The equilibrium constant of a solution of compound **5**, equilibrated at −60 °C, has been measured by integration of the corresponding $^{31}P\{^1H\}$ resonances under conditions of complete spin relaxation and has been found to be K = [**5B**]/[**5C**] ≃ 1.7. No correction for the small amount of **5A**, in fast equilibrium with **5C**, has been made. Obviously these results confirm that the C–H···Mo interaction in **5C** is structurally and thermodynamically competitive with the η^2-acyl coordination **5B**.

(13) Under the conditions used, the changes observed in the NMR spectra with temperature are reversible and appear to be independent of the concentration of the sample and of the solvent used (toluene, acetone, dichloromethane, and tetrahydrofuran).

Mo-bound methyl group. (ii) The coupling constant between the methyl protons and the ^{31}P nuclei increases from 1.8 Hz at −20 °C (at lower temperatures the corresponding signal is unresolved) to 3.0 Hz at 20 °C. For comparison, in the structurally characterized methyl-tungsten complexes[5b,c] $W(CH_3)(L\text{-}L)(CO)_2(PMe_3)_2$ (L-L = acac, S_2CNR_2, S_2COR) this coupling ranges from 3.5 to 8 Hz. (iii) The solution IR spectrum of **4** (20 °C) is more complex than those of **1**–**3** and shows, in addition to bands due to the carbonyl functionalities in the agostic and η^2-acyl isomers, two absorptions at ca. 1912 and 1836 cm^{-1} which can be tentatively assigned to the terminal carbonyl ligands in the methyl dicarbonyl species $Mo(CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)_2(PMe_3)_2$.

In conclusion, our results indicate that in the system under investigation there are small energy differences among the isomeric structures A, B, and C, so that both types of acyl coordination, B and C, are kinetically and thermodynamically accessible from their isomeric alkyl–carbonyl structure A. Since most of the acyl complexes of molybdenum known to date have η^2 structures while the only known agostic acyls are those discussed in this paper, it seems that the C–H···Mo interaction becomes structurally and thermodynamically competitive only in the presence of strongly electron releasing ligands such as the dithiocarbamates and xanthates. Note however that the analogous tungsten complexes have alkyl–carbonyl structures.[5] Therefore it is clear that very subtle electronic effects must be responsible for the observation in the present system of the three isomeric structures A, B, and C.

Registry No. 2, 133400-33-6; **3**, 133400-32-5; **4**, 133400-34-7; **5A**, 133400-29-0; **5B**, 133400-30-3; **5C**, 133400-31-4; $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$, 89727-04-8; $NaS_2CN\text{-}i\text{-}Pr_2$, 4092-82-4; $NaS_2CNC_5H_{10}$, 873-57-4; NaS_2COMe, 6370-03-2; $NaS_2CO\text{-}i\text{-}Pr$, 140-93-2.

On the Transition States of Electrophilic Radical Additions to Alkenes

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Carbon-centered radicals are nucleophilic or electrophilic species, depending upon the substituent at the radical center. Electron-donating substituents like alkyl or alkoxy groups increase the nucleophilicity[1] of radicals whereas electron-withdrawing substituents like ester or nitrile groups augment their electrophilic[2] behavior. Calculations for a variety of cases have shown that nucleophilic radicals approach the olefinic carbon atoms at angles between 104° and 108° at the UHF/3-21G level.[3] Figure 1 shows the geometry for the addition of the methyl radical to ethylene at the UHF/6-31G* level.[3b]

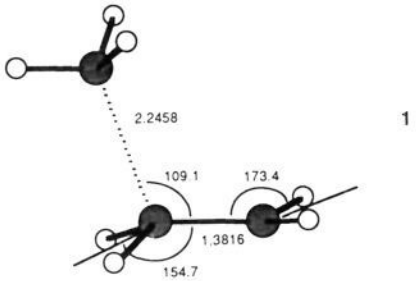
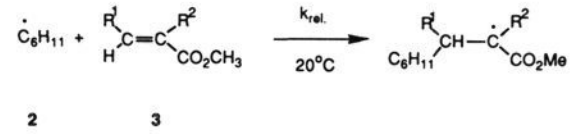
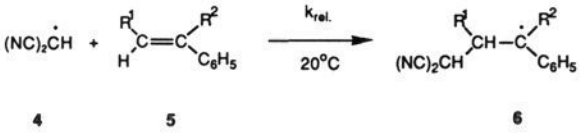


Figure 1. UHF/6-31G* transition state for the addition of the methyl radical to ethylene.

Scheme I



Scheme II



Scheme III

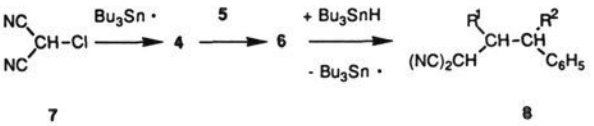


Table I. Values of k_{rel} for Reaction Depicted in Scheme II

R^1	R^2	k_{rel}	R^1	R^2	k_{rel}
H	H	≡1000	H	H	≡1000
H	CH_3	820	CH_3	H	110
H	C_2H_5	360	C_2H_5	H	20
H	$i\text{-}C_3H_7$	120	$i\text{-}C_3H_7$	H	<1

Transition state **1** is also in accord with substituent effects on rates. Thus, in addition of the nucleophilic cyclohexyl radical **2** to substituted acrylates **3** (Scheme I), alkyl groups R^2 reduce the rate of addition only slightly, but alkyl groups R^1 at the attacked olefinic carbon atom exert huge rate-decreasing effects.[1b] Absolute rate measurements for reactions of *tert*-butyl radicals with various alkenes exhibit comparable results.[4]

These unequal substituent effects point to unsymmetrical transition states **1** in which only the attacked olefinic carbon atom deviates considerably from its ground-state geometry. Therefore substituents at this center exhibit large steric effects. Normally nucleophiles and electrophiles add to carbonyls and alkenes with quite different geometries.[5] It was therefore of interest to determine to what extent electrophilic and nucleophilic radicals differ in their transition-state geometries.

We have now shown that addition reactions of electrophilic malononitrile radical **4** with substituted styrenes **5** (Scheme II, Table I) give similar results to nucleophilic radicals, providing the first experimental evidence for the transition-state geometry of electrophilic radical addition.[5]

Substituents R^1 at the attacked carbon atom of alkenes **5** exert much larger rate-decreasing effects than adjacent substituents R^2.[6]

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