Preparation, Structure, and Chemistry of (*O*-Acyl imidato)- and (*O*-Alkyl imidato)carbene Pentacarbonyl Complexes of Chromium

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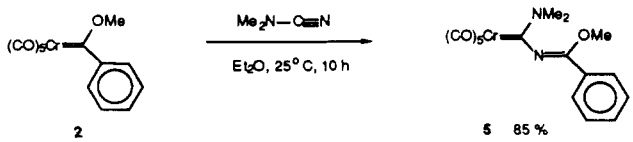
The first examples of the insertion of organonitriles (R^2CN; R^2 = Me, Ph, *n*-Pr, *i*-Pr, *t*-Bu, CH_2Ph, *p*-$MeOC_6H_4$, 2-furyl) into the metal–carbon bond of heteroatom-stabilized Fischer carbene complexes ($(CO)_5CrC(OMe)R^1$; R^1 = Ph, Me) to give imidatocarbene complexes are described. The structures of the imino complexes **14** and **12** from the reaction of the phenyl complex **2** with benzonitrile and *tert*-butyl cyanide were determined by X-ray diffraction and found to have C–N–C angles of 153° and 174°, respectively, indicating that the nitrogen plays a significant role in stabilizing the carbene carbon of the imino carbene complex. The kinetic methylation of the imino complex **13** from the reaction of the phenyl complex **2** and benzyl cyanide gave a 14:1 mixture of separable diastereomers **38a** and **38b** which is a consequence of an axis of chirality about the C–N–C 2-azaallenyl linkage. The stereochemistry of the major diastereomer **38a** was determined by X-ray diffraction analysis which reveals that the dihedral angle about the C–N–C linkage is nearly perpendicular at 94.1°. The first example of the reversible insertion of a nitrile into a transition-metal carbene complex was found in the investigation of the reaction of the *tert*-butyl imino complex **12** with 1-pentyne. The first examples of (*O*-acyl imidato)carbene complexes are described which are prepared by the double acylation of aminocarbene complexes. The two methods described for this double acylation are the acylation of anions stoichiometrically generated from amino complexes and the acylation in the presence of triethylamine and 4-(dimethylamino)pyridine. The solid-state structure of the *O*-acyl imidate complex **32** was found to be quite similar to that of the *O*-alkyl imidate complexes. Crystal data for **32**: space group $P2_1/n$, Z = 4, a = 13.268 (5) Å, b = 11.573 (4) Å, c = 15.951 (7) Å, β = 109.20 (2)°, R = 0.059, and R_w = 0.056 for the 3032 reflections with $F_o > 2.33\sigma(F_o)$. Finally, an optimized procedure was found for the selective mono-alkylation of the phenylaminocarbene complex **21**.

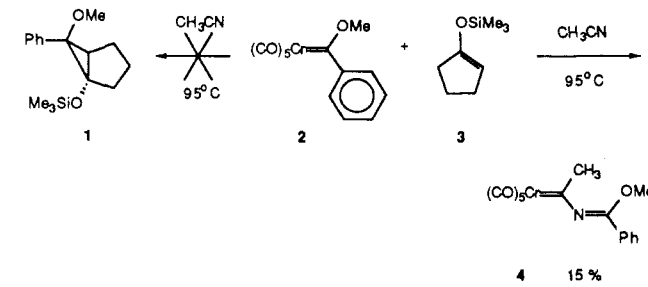
The cyclopropanation of a transition-metal carbene complex was first reported by Fischer 15 years ago. He observed that electron-rich olefins could be cyclopropanated with group 6 pentacarbonyl carbene complexes in good yield.[2] The chromium complex **2** was reported to react with ethyl vinyl ether to give a 60% yield of the cyclopropanation product (3:1 mixture of diastereomers) under a hundred atmospheres of carbon monoxide. We have recently reported that silyl enol ethers are much more efficacious in cyclopropanation reactions with **2** as they give higher yields and higher stereoselection.[3] Encouraged by these results, we attempted the cyclopropanation of the trisubstituted silyl enol ether **3** with the chromium phenylcarbene complex **2**. Under moderate conditions there was no reaction observed, however, when more forcing conditions were employed and the two starting materials were heated to 95 °C in acetonitrile, none of the anticipated cyclopropane **1** was detected, and all that could be isolated from the reaction mixture was the imidate carbene complex **4** which had incorporated a molecule of the solvent.

This type of insertion of a carbon–nitrogen triple bond into the carbene–metal bond had been previously observed with cyanamides,[4] cyanates,[5] and thiocyanates.[5] These reactions are in general very rapid as indicated for the reaction of **2** with dimethylcyanamide which occurs at room temperature to give the insertion product **5** in which the carbene carbon is stablized by two nitrogen atoms.[4a,c]



2 **5** 85 %

Scheme I



1 **2** **3** **4** 15 %

At the time there had not been any reports of the insertion of organonitriles, but shortly thereafter, H. Fischer reported the insertion reactions of organonitriles into non-heteroatom-stablized group 6 pentacarbonyl carbene complexes.[6] The reactions of group 6 carbene complexes and silyl nitriles has been reported but takes a different course.[7] A few other examples of imine-stablized group 6 carbene complexes have been reported as products from reactions that do not involve insertions of nitriles.[8] The reaction

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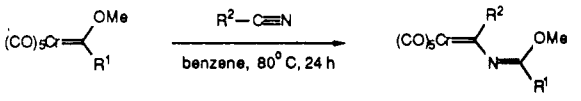
Table I. Reactions of Chromium Complexes 2 and 9 with Organonitriles[a]



entry	starting complex	R^1	R^2	reaction time	insertion product	% yield	% recov of starting	total mass bal
1	**2**	Ph	Me	24 h	**4**	36	38	74
2		Ph	Me	5 days	**4**	54[b]	ND	
3		Ph	*n*-Pr	24 h	**10**	51	31	82
4		Ph	*i*-Pr	24 h	**11**	73	9	82
5		Ph	*i*-Pr	6 h	**11**	39	35	74
6		Ph	*i*-Pr	24 h	**11**	68[c]	12	80
7		Ph	*i*-Pr	6 h	**11**	46[d]	12	58
8		Ph	*t*-Bu	24 h	**12**	38	34	72
9		Ph	*t*-Bu	5 days	**12**	53[e]	ND	
10		Ph	CH_2Ph	24 h	**13**	72	7	79
11		Ph	Ph	24 h	**14**	85	0	85
12		Ph	*p*-$MeOC_6H_4$	4 days	**15**	93[f]	0	93
13		Ph	2-furyl	24 h	**16**	92	0	92
14	**9**	Me	Ph	38 h	**17**	68[g]	ND	

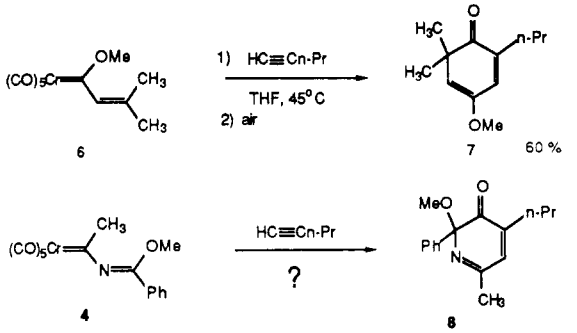
[a] Unless otherwise specified all reactions were carried out at 0.13 M in **2** or **9** in benzene with 14 equiv of nitrile at 80 °C for the indicated time. [b] 10 equiv of nitrile. [c] THF as solvent. [d] Isobutyronitrile as solvent. [e] 5 equiv of nitrile. [f] 2.4 equiv of nitrile. [g] 3 equiv of nitrile and 0.7 M in **9**.

of titanium carbene complexes with nitriles occurs with opposite regiochemistry in the addition of the nitrile to the metal–carbene carbon bond.[9]

It is interesting to consider the possible synthetic applications of imidatocarbene complexes of the type **4** in synthetic organic chemistry. One reaction of imidatocarbene complexes that can be anticipated is the reaction with alkynes to produce 5-azacyclohexa-2,4-dienones. The imidate complex **4**, for example, can be considered to be a 2-aza analogue of an alkenyl carbene complex. It has previously been shown that β,β-disubstituted alkenyl complexes of the type **6** will undergo a cyclohexadienone annulation with alkynes and, for the particular case shown with 1-pentyne, give rise to the cyclohexa-2,4-dienone **7**.[10] Before pursuing the reactions of imidatocarbene complexes with alkynes, it was necessary to find conditions under which the efficiency of the nitrile insertions are improved.

Preparation of (*O*-Alkyl imidato)carbene Complexes from Nitrile Insertions. After a survey of a number of solvents and conditions it was found that the optimal conditions for the reactions of organonitriles with chromium carbene complexes is in benzene at 80 °C for 24 h with excess nitrile.[11] As indicated by the data in Table I, a variety of imidate complexes can be made in moderate to excellent yields from both aliphatic and aryl cyanides. Successful insertion reactions include those with aryl- and alkyl-substituted carbene complexes. The mass balance of these reactions is quite good. There is apparently not much difference between benzene and THF as solvent in these reactions as indicated by the entries 4 and 6. Not unexpectedly, the reaction appears to be faster in nitrile solvent than in benzene (entries 5 and 7), but the total mass balance is lower in nitrile solvent. We suspect that this is due to competing cleavage of the carbene ligand (in either the starting complex **2** or the product imidate complex **4**) by the nitrile[6] and that this is why the reaction in Scheme I gave only a 15% yield of the insertion product **4** and that in benzene solvent with only a slight excess of

Scheme II



acetonitrile that much higher yields can be obtained (entries 1 and 2). It should also be noticed that aryl cyanides go to completion, whereas alkyl cyanides were found difficult to drive to completion. This may be a result of the fact that several of the insertion reactions indicated in Table I are in fact in equilibrium as will be demonstrated for the reaction with *tert*-butyl cyanide (vide infra).

The reaction of the *tert*-butyl imidate complex **12** with 1-pentyne produced a surprise. None of the expected annulated product **19** was observed, but rather this reaction produced only the naphthoquinone **18** after an oxidative workup with ceric ammonium nitrate. This result suggests that the insertion of *tert*-butyl cyanide into the chromium–carbon bond of the phenylcarbene complex **2** is reversible since the quinone **18** is a known product from the reaction of complex **2** with 1-pentyne.[12] It was established that the imidate complex **12** is in equilibrium with *tert*-butyl cyanide and the phenyl complex **2** and that the equilibrium favors the phenyl complex **2** by 4.6:1 at 80 °C. This equilibrium value can be reached from either side in 36 h in benzene and was determined in each case by the isolation of **2** and **12** where the total mass recovery of complexes **2** and **12** after equilibrium is between 85 and 87% for each experiment. This is the first time that the insertion of a nitrile into the metal–carbon bond of a

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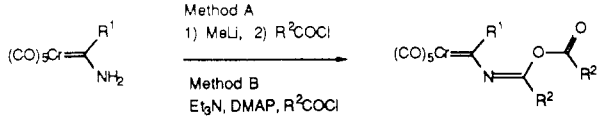
(12) (a) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. (b) Dötz, K. H.; Muhlemeier, U.; Schubert, U.; Orama, O. *J. Organomet. Chem.*, **1983**, *247*, 187.

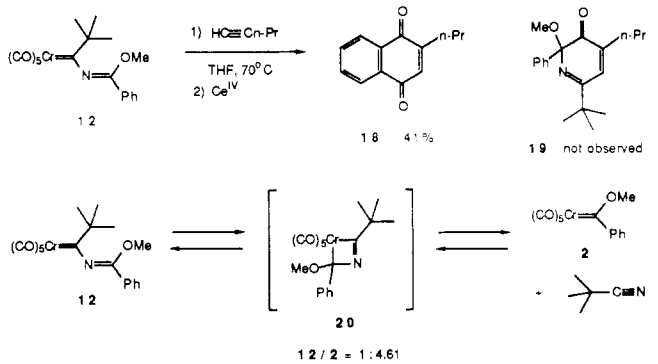
Table II. Double Acylation of Aminocarbene Complexes[a]



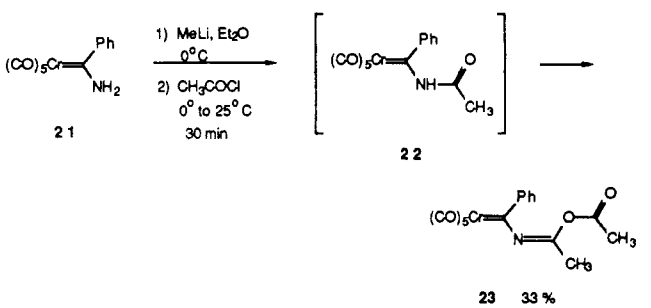
entry	starting complex	R^1	R^2	method[a]	temp, °C	time	imidate complex	% yield	% recov start mat
1	**21**	Ph	Me	A	25	30 min	**23**	33[b]	47
2				B	25	14 h	**23**	<2[c]	19
3				B	25	14 h	**23**	<2[d,e]	53
4		Ph	Ph	A	25	1 h	**29**	36	58
5				B	25	15 min	**29**	97	0
6	**24**	Me	Me	A	25	1 h	**30**	19	70
7				B	25	2 h	**30**	0	0[f]
8				B	55	5 days	**30**	0	0[e]
9	**25**	*i*-Pr	Ph	A	25	1 h	**31**	50	48
10	**26**	*t*-Bu	Ph	A	25	1 h	**32**	37	45
11				B	25	3 h	**32**	93	0
12		*t*-Bu	*p*-ClC_6H_4	B	25	3 h	**33**	89	0
13				B	60	6 h	**33**	45	32[e]
14		*t*-Bu	*p*-$MeOC_6H_4$	A	25	1 h	**34**	41	62
15				B	25	3 days	**34**	77	18
16		*t*-Bu	Me	A	25	1 h	**35**	28	52
17				B	55	3 days	**35**	0	40[g]
18				B	25	3 days	**35**	17	59[h]
19	**27**	$-(CH_2)_3C{\equiv}CCH_3$	Me	A	25	1 h	**36**	42	39

[a] Method A: i, MeLi (1 equiv), Et_2O, 0 °C, 20 min; ii, R^2COCl (2.2 equiv), 0–25 °C. Method B: Et_3N (8 equiv), DMAP (0.06–0.2 equiv), R^2COCl (2.2 equiv), CH_2Cl_2. [b] **22** obtained in 3% yield. [c] **22** obtained in 27% yield and DMAP pentacarbonylchromium **37** was obtained in 12% yield. [d] **22** obtained in 23% yield. [e] DMAP deleted from the reaction. [f] Ac_2O instead of AcCl, 0.48 equiv of DMAP employed, 36% yield (based on **24**) of DMAP pentacarbonylchromium **37** was isolated. [g] DMAP pentacarbonylchromium **37** was isolated in 7% yield (based on **26**). [h] Ac_2O instead of AcCl, 8% yield (based on **26**) of DMAP pentacarbonylchromium **37** was isolated.

Scheme III



Scheme IV



carbene complex has been shown to be reversible. While we have not studied the reversibility of these reactions in detail, it has been found that the insertions of *n*-butyronitrile and isobutyronitrile are reversible; however, the equilbrium constants were not measured.

In an unrelated effort, several years ago we had attempted to prepare the imide carbene complex **22** by acylation with acetyl chloride. When the phenyl amino complex **21** was stoichiometrically deprotonated with methyllithium and then treated with 1 equiv of acetyl chloride, the product that was produced from the reaction was found to be the double-acylated imidate carbene complex **23** in 33% yield. Since the formation of **23** in this reaction requires that **22** be deprotonated by the anion of **21**, the maximum yield of **23** is 50% and accordingly the isolation of **23** was accompanied with the recovery of 47% of the starting material **21**. We have recently gone back and repeated this reaction and found that a small amount (3%) of **22** can be isolated from this reaction under these conditions. The *O*-acyl imidate complexes are a new class of carbene complexes that have not been previously reported[13] but which at the time we did not pursue. Upon realizing the failure of the annulation of the imidate complex **12** our interest in pursuing the chemistry of the (*O*-acyl imidato)carbene complexes of the type **23** was rekindled. It can be anticipated that the deinsertion of a nitrile from an O-acyl imidate complex of the type **23** would be less favorable than for imidate complexes of the type **12** since *O*-acyloxy carbene complexes[14] are much less stable than *O*-alkyl complexes.

Preparation of (*O*-Acyl imidato)carbene Complexes via Double Acylation. The results from the evaluation of two different methods for the preparation of (*O*-acyl-imidato)carbene complexes are presented in Table II. Method A involves the acylation of the stoichiometrically generated anion of an aminocarbene complex analogous to the method that was employed in the inadvertent preparation of the bis-acylated complex **23**. This method

(13) The preparation of *O*-acyl imidate complexes by this method has also been observed by Professor L. Hegedus. We thank Professor Hegedus for the advanced communication of his results which are described in the preceding paper in this issue A report describing the preparation of *O*-acyl imidate complexes by this method appeared in the literature while this manuscript was in review; Aumann, R.; Hinterding, P. *Chem. Ber.* **1989**, *122*, 368.

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has the disadvantage discussed above, that is, the reaction cannot be driven past 50% completion. However, in most of the reactions in Table II a high recovery of the starting material was observed and thus can be recycled. Despite this disadvantage, this method does have some utility, particularly for the *O*-acyl imidate complex **30**, which can only be prepared by this method, and complex **35**, which is best prepared by this method.

It was readily apparent that a superior preparative method for (*O*-acyl imidato)carbene complexes would be one that involved the use of 2 equiv of a base that could tolerate the presence of an acid chloride or other suitable acylating agents. A number of systems and reagents have been developed for acylations, and in the case of alcohols the most efficacious method involves the use of triethylamine as stoichiometric base in the presence of a catalytic amount of (*p*-dimethylamino)pyridine (DMAP).[15] This method (B) was highly successful in the direct preparation of a number of the *O*-acyl imidate complexes listed in Table II and in particular provides the complexes **29**, **32**, and **33** in yields of 90% or greater. As has been observed in the acylation of alcohols,[15] DMAP greatly increases the rate of bis-acylation of the *tert*-butylaminocarbene complex **26** compared to the acylation of **26** with triethylamine alone (entries 12 and 13). The typical procedure for method B involves the utilization of excess triethylamine (8 equiv) with a catalytic amount of DMAP (0.06–0.2 equiv). For reasons that we do not yet understand, the bis-acylation of amino carbene complexes catalyzed by DMAP works well for acylation with benzoyl chloride but is of little value for acylation with acetyl chloride. The only success at all in this regard, was for the preparation of complex **35** (entry 18) in which acetic anhydride was substituted for acetyl chloride. The reasons for the limited success in this case may be related to those that have been envoked to account for the greater rates of acylation of alcohols with acetic anhydride over acetyl chloride under DMAP catalysis.[15b] The preparation of the *O*-acyl imidate complex **31** has only been attempted with method A; however, given the data in Table II it is to be expected that method B will be the method of choice for this complex. Likewise the functionalized *O*-acyl imidate complex **36** has only been prepared by method A; however, from the data in Table II, it can be anticipated that method B will not be useful for the preparation of this complex, and ultimately the optimum procedure for the preparation of this complex may involve sequential acylations (vide infra).

When the catalytic acylation procedure involving DMAP catalysis that had been successful for the preparation of a number of complexes in Table II was extended to the (*O*-acyl imidato)carbene complex **23** that we had first prepared (Scheme IV), it was a surprise to find that the mono-acylated imide carbene complex **22** was the major product of the reaction (Scheme V). None of the bis-acylated (*O*-acyl imidato)carbene complex **23** was produced in this reaction. Workup of this reaction also provided an 11% recovery of **21** and a 12% yield (based on **21**) of DMAP pentacarbonylchromium **37**. As mentioned above we do not understand the reasons why acylations with amine bases fail with acetyl chloride, but the isolation of DMAP pentacarbonylchromium **37** suggests that displacement of the carbene ligand from the metal may be occurring at the mono or bis-acylated complexes more readily when acetyl chloride is employed. Of the examples listed in Table II, DMAP cleavage products were observed only for acetyl chloride (entries 2, 7, 17, and 18) and not for reactions with benzoyl chloride. However, this is not the only explanation since no improvement is observed when acylation is repeated in these cases with triethylamine in the absence of DMAP (entries 3, 8). In the acylation of **21** with acetyl chloride, if DMAP is deleted from the reaction shown in Scheme V, under the same conditions and time period the reaction produces a 23% yield of the mono-acylated imide complex **22** and a 53% recovery of the amino complex **21**. The mono-acylated imide complexes of the type **22** may have interesting applications in organic synthesis, but we have not optimized the mono-acylation process for any of the amino complexes listed in Table II except for the phenyl amino complex **21**. The mono-acylation of **21** can be effected in 86% yield in 25 min at room temperature with acetic anhydride and DMAP. It may well be that the best method for the double acylation of amino complexes with acetyl chloride will prove to be a stepwise process.

Scheme V

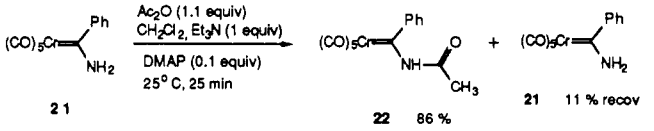

Table III. ^{13}C NMR Data of (*O*-Acyl imidato)- and (*O*-Alkyl imidato)carbene Complexes[a]

complex	$C_{carbene}$	C_{M-CO} trans	C_{M-CO} cis	$C_{carbonyl}$	$C_{imidate}$
		O-Alkyl Imidate Complexes			
4	254.43	219.96	213.98		134.23
10	257.38	223.36	217.63		138.59
11	258.79	223.32	217.66		141.02
12	257.41	223.13	218.21		137.00
13	252.22	223.33	217.59		140.16
14	260.11	223.96	217.44		138.56
15	253.15	223.74	218.05		137.30
16	244.55	224.29	217.95		137.99
17	261.26	224.15	217.51		133.67
38a	256.78	223.14	217.48		139.30
38b	253.27	223.17	217.61		140.35
		O-Acyl Imidate Complexes			
23	252.36	224.27	217.02	166.32	130.01
29	252.12	224.22	216.87	162.20	129.86
30	253.42	223.73	217.00	165.99	129.09
31	252.65	223.66	216.98	162.31	126.23
32	250.10	223.37	217.44	162.14	130.21
33	252.44	223.11	217.26	161.31	129.47
34	250.05	223.43	217.57	161.74	130.67
35	249.33	223.28	217.57	166.24	129.55
36	250.48	223.63	217.02	166.08	130.85

[a] Shifts in ppm from TMS in $CDCl_3$.

Spectral Data of (*O*-Alkyl imidato)- and (*O*-Acyl imidato)carbene Complexes. The initial analysis of the routine spectral data for the products of the bis-acylation of the amino complexes in Table III leaves some uncertainty as to whether these products are in fact those that result from sequential N- and O-acylations and have structures of the type **32** or are those that result from double acylation on nitrogen to give structures of the type **32b**. The proton NMR of the product from the reaction of amino complex **26** and benzoyl chloride is consistent with both of the structures **32** and **32b**. The IR spectrum of this product has a carbonyl stretching frequency of 1755 cm^{-1}, which is consistent with the stretching frequency expected for the carbonyl in structure **32** in which the

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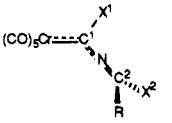
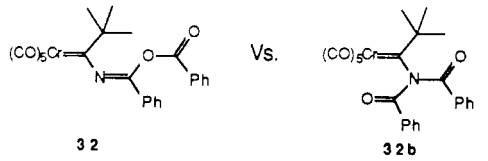
Table IV. Selected Bond Distances (Å) and Angles (deg) of Imidate Complexes



compd	X^1	X^2	R	$\angle C^1\text{-}N\text{-}C^2$	$\angle X^1\text{-}C^1\text{-}N$	∠dihedral[a]	Cr–C^1	C^1–N	C^2–N
39	NMe_2	OMe	Ph	134.6	113.0		2.135	1.342	1.264
14	Ph	OMe	Ph	152.7 (3)	113.4 (2)	92.3	2.112 (3)	1.297 (3)	1.264 (4)
12	t-Bu	OMe	Ph	174.2 (4)	113.0 (3)	92.9	2.147 (4)	1.268 (5)	1.265 (5)
32	t-Bu	OCOPh	Ph	169.6 (3)	113.1 (5)	85.4	2.126 (5)	1.271 (7)	1.268 (7)
38a	CH(Me)Ph	OMe	Ph	165.6 (3)	113.4 (2)	94.1	2.090 (3)	1.280 (4)	1.264 (4)

[a] Angle between the planes defined by Cr–C^1–X^1 and R–C^2–X^2.

Scheme VI

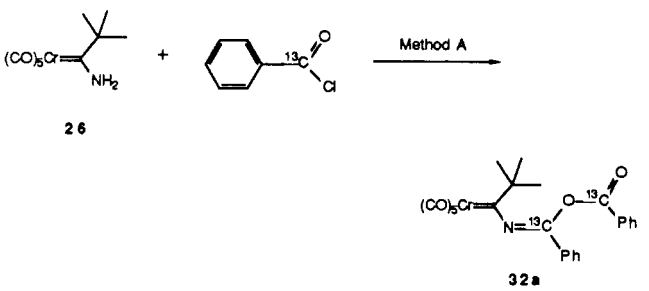


32 Vs. **32b**

environment of the carbonyl can be likened to an anhydride and is not consistent with that expected for the structure **32b** in which the carbonyl is part of an imide function in which the stretching frequency would be expected to be similar to that of 1644 cm^{-1} observed for the mono-acylated complex **22**. The initial analysis of the ^{13}C NMR spectrum proved to be less convincing than the IR spectrum that the structure was in fact **32**. The disturbing aspect of the ^{13}C NMR spectrum originally obtained for this product is that it was one carbon short for both the structures **32** and **32b**. The observed ^{13}C NMR spectrum could be accommodated by structure **32b** if it is assumed that both of the carbonyl carbons have the same chemical shift of δ = 162.14 ppm. This is not considered to be too likely since it is observed in amino complexes that there is a substantial barrier to rotation about the nitrogen–carbene carbon bond.[16] The barrier to rotation about the nitrogen–carbene carbon bond in **32b** would be expected to be lower than for a typical amino complex, but it is difficult to imagine that it would be lowered to the degree necessary to allow the carbonyl carbons to interchange on the NMR time scale. It was judged more likely that one of the carbons in the ^{13}C NMR spectrum was not observed.

It was suspected that the missing absorption in the ^{13}C NMR spectrum of **32** was the imidate carbon, and to confirm this the ^{13}C-labeled *O*-acyl imidate complex **32a** was prepared from benzoyl chloride that was 99+ atom % enriched in ^{13}C at the carbonyl carbon. There were two absorptions in the ^{13}C NMR spectrum of **32a** that were enhanced due to enrichment, and these were observed at δ = 162.14 and δ = 130.21 ppm. The absorption at δ = 162.14 then can be assigned as the carbonyl carbon of **32** and the absorption at δ = 130.21 can be assigned as the imidate carbon. The imidate carbon in these complexes is less intense than other quaternary carbons but can be definitively identified if sufficient sample is used to obtain a high signal to noise ratio. The chemical shift of the carbene carbon at δ = 250.10 ppm was more in line with that expected for structure **32** in which the lone pair is relatively free to delocalize onto the carbene carbon and not so much in line for the expected chemical shift of the carbene carbon of **32b** in which the lone pair would be much less available for such delocalization. This expectation can be calibrated with the observation that the phenyl amino complex **21** has the carbene carbon at δ = 282.9 ppm, and the mono-acylated product **22** has the carbene carbon at δ = 317.54 ppm. The latter chemical shift is in acetone-d_6 and the former is in chloroform-*d*; however, the comparison should be valid since we have found that the shift of the carbene carbon in these complexes does not vary (<3 ppm) from acetone to chloroform. Thus the conclusion to be drawn from all of the spectral data taken together is that the bis-acylation has occurred on nitrogen and on oxygen to generate (*O*-acyl imidato)-carbene complexes. The chemical shifts of the imidate and carbene carbons of the bis-acylated complexes are included in the ^{13}C NMR data presented in Table III and reveal that all of these complexes have the *O*-acyl imidate structure. The chemical shifts of the imidate and the carbene carbons of the *O*-acyl imidate complexes are very similar to those of the *O*-alkyl imidate complexes prepared by nitrile insertion.[11]

Scheme VII

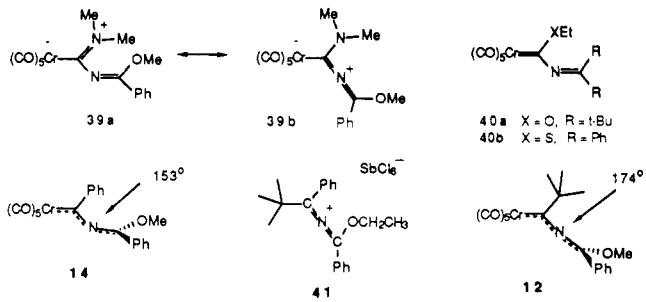


26 **32a**

Solid-State Structures of (*O*-Acyl imidato)- and (*O*-Alkyl imidato)carbene Complexes. The solid-state structures of a few imidate carbene complexes that were derived from the insertions of cyanamides,[4a,c] cyanates,[8a] and thiocyanates[5] had been previously reported. The first was for the imidate complex **39** derived from the reaction of complex **2** with dimethylcyanamide.[4a,c] The C–N–C bond angle in complex **39** about the imidate nitrogen is of interest because it should reflect on the relative importance of the two different nitrogen substituents in stabilizing the carbene carbon. The observed angle of 134° suggests that the resonance structure **39a** is more important than **39b** and that the amino nitrogen carries the burden of stabilizing the carbene carbon. The imidate nitrogen would be expected to be much more greatly involved in the stabilization of the complex where the amino nitrogen of **39** is replaced by a group with a lesser propensity for electron donation via resonance. This expectation has been realized in the structures of complexes **40a** (X = O[8a]) and **40b** (X = S[5]), where in both cases the C–N–C angle of the imidate ligand is widened with respect to that for **39** (172° for **40a** and 149° for **40b**). We have

(16) For a general review of the field of carbene complexes, see: Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984.

Scheme VIII



previously reported the structures of **14** and **12** where this angle widening was also found for imidate complexes bearing a carbon as the other carbene carbon substituent.[11] Selected structural data for compounds **14** and **12** and three imidate complexes are presented in Table IV. In the benzonitrile insertion product **14** the angle has widened to 153°, and in the structure of the *tert*-butyl cyanide insertion product **12**, where π-delocalization to the carbene carbon is impossible, the C–N–C linkage is nearly linear at 174°.[11] Examination of intramolecular contacts for the *tert*-butyl imidate complex **12** suggests that the nearly linear C–N–C bond angle is not being determined by any intramolecular steric effects. A rehybridization of the nitrogen in complex **12** would be expected in order to accommodate the near linearity of the C–N–C angle, and further, as revealed by the angle between the planes defined by Cr–C^1–X^1 and by R–C^2–X^2 there is an axis of chirality about the C–N–C linkage. This structural feature is observed for the 2-azaallenyl cation **41** in which carbon–nitrogen bond rotation is slow enough that the methylene protons of the ethoxy group are diastereotopic but coalesce slightly above room temperature in the ^{1}H NMR.[12]

The CNC bond angle in the *O*-alkyl imidate complexes **12** and **14** reveals that there is considerable delocalization of the imidate nitrogen lone pair onto the carbene carbon. The crystal structure of the O-acyl imidate complex **32** was undertaken to determine the relative extent to which the lone pair of the imidate nitrogen in an (*O*-acyl imidato)-carbene complex could be delocalized to the carbene carbon and also as a final verification of structure for this compound. Selected structural data for **32** are presented in Table IV, the ORTEP of **32** is presented in Figure 1, and the details of the X-ray diffraction study are included in the supplementary material. Replacing the methoxyl group in **12** with the benzoyl group has remarkably little effect on the structural parameters listed in Table IV. It is also remarkable that the bond angle X^1–C^1–N is virtually independent of the nature of X^1. The only structural parameters that vary with the nature of X^1 are the bond angle C^1–N–C^2 and the bond length C^1–N which vary as expected in accord with the ability of X^1 to delocalize electrons onto the carbene carbon.

Diastereoselective Alkylation of an Imidatocarbene Complex. A question of concern in establishing the synthetic potential of imidate carbene complexes is whether there is sufficient hinderance to rotation about the C–N–C bonds such that the axis of chirality can serve to induce asymmetry in the reactions of these complexes. We were encouraged in this regard by the fact that the methylene protons of the phenylacetonitrile insertion product **13** are diastereotopic on the ^{1}H NMR time scale. More convincingly, when the methylene group of complex **13** is deprotonated with *n*-butyllithium and methylated, a mixture of separable diastereomers is obtained in 73% yield.[17,18] The kinetic ratio obtained from the crude ^{1}H

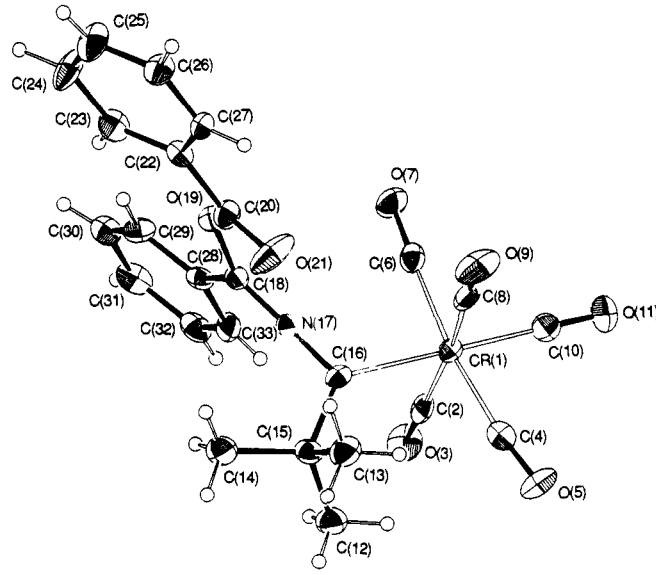
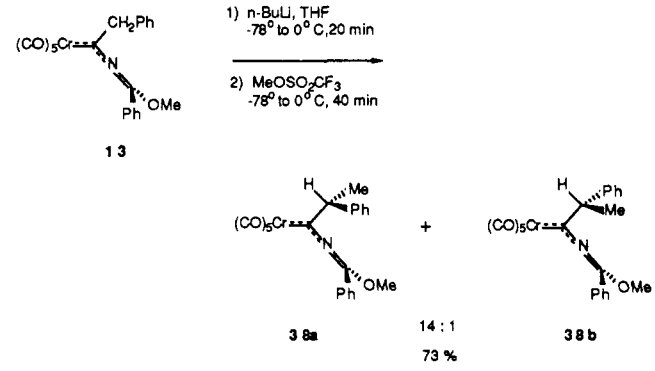


Figure 1. ORTEP drawing of compound **32**.

Scheme IX



NMR is 14:1, and the isolated ratio of the diastereomers from preparative TLC is 9:1. Each diastereomer will slowly epimerize at room temperature in a chloroform solution, and a thermodynamic mixture of 1:1.65 in favor of **38b** can be obtained after 10 days starting from either diastereomer.[19]

The major kinetic isomer **38a** does not epimerize in the solid state, and the structure of this diastereomer was determined by an X-ray diffraction analysis.[11] The C–N–C bond angle in this complex is 165.6° (Table IV) which is intermediate between the angles for the complexes **12** and **14**. The dihedral angle about the C–N–C azaallenyl linkage is nearly perpendicular at 94.1° (3), which is the angle between the two planes defined by CR(1)–C(12)–C(23) and by O(15)–C(14)–C(17). The reasons for the kinetic diastereoselection in favor of the particular stereoisomer **38a** is not readily evident at this time. In this alkylation reaction the two key issues for consideration are the preferred conformation about the $C_{carbene}$–$C_{benzylic}$ bond of the anion generated from **13** and the direction of approach of the electrophile. Upon first consideration the stereoselectivity of the reaction can be accounted for by the preferred approach of the electrophile syn to the methoxy group on the basis of the steric differences between methoxyl and phenyl, if it is assumed that the preferred conformation of the anion is that in which the H–C–Ph

(17) Casey, C. P. *J. Organomet. Chem. Libr.* **1976**, *1*, 397.
(18) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.
(19) The mass recovery of the 1:1.65 mixture of **38a** and **38b** after 10 days is 77% starting from **38b**.

plane is parallel with the Cr–C–N plane and with the remaining hydrogen of the methylene syn to the metal. This consideration is weakened not only by the distances between the benzylic carbon and the methoxyl and phenyl groups but also by the expectation that the geometry of the azaallenyl substituent of the carbene carbon may be dramatically affected by the delocalization of the electrons of the benzylic carbanion generated from **13** onto the metal center. Further information concerning the source of the stereoselectivity in the alkylation of **13** may have to await structural data for the anion generated from **13**. Although the source of the stereoselectivity of the alkylation reaction cannot be determined with the present data, the fact that specific stereoisomers of imidatocarbene complexes can be generated and isolated, by virtue of the axis of chirality about the azaallenyl linkage, may prove to be significant in the development of the applications of these complexes to synthetic organic chemistry.

Conclusion

It has been demonstrated that (*O*-alkyl imidato)- and (*O*-acyl imidato)carbene complexes can be prepared in good yields in a relatively straightforward manner from readily available alkoxy or amino carbene complexes. The solid-state structures of both *O*-alkyl and *O*-acyl imidate complexes reveal that there is an axis of chirality about the C–N–C azaallenyl linkage of the imidate substituent of the carbene ligand which is due to the considerable delocalization of the nitrogen lone pair onto the carbene carbon. In the diastereoselective alkylation of the benzyl complex **13**, it was demonstrated that the chiral axis about the azaallenyl function is configurationally stable since the two diastereomers **38a** and **38b** could be isolated. The degree of diastereoselection in this alkylation (14:1) is encouraging enough to prompt the investigations of the stereoselection relative to the azaallenyl linkage in other reactions of these complexes. The *O*-alkyl imidate complexes can be prepared by insertion reactions of nitriles and alkoxycarbene complexes of chromium. The insertion of the nitrile was shown to be reversible in some instances, and this was found to be a limitation in the reaction of the (*O*-alkyl imidato)carbene complexes and alkynes. It is anticipated that the (*O*-acyl imidato)carbene complexes which are prepared by the double acylation of aminocarbene complexes will not suffer a deinsertion of a nitrile upon thermolysis and thus will be more useful in reactions with acetylenes. The investigation of the applications of (*O*-acyl imidato)carbene complexes can now be pursued, and the results will be reported at a future date. Finally, a method has been developed for the efficient monoacylation of amino complexes, and the resulting imidocarbene complexes are now available in quantity which should greatly facilitate the investigation of their chemistry.

Experimental Section

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl immediately prior to use. Anhydrous diethyl ether was obtained from containers opened within 48 h of use or freshly distilled from benzophenone ketyl. Benzene was stored over activated 4-Å molecular sieves for at least 48 h before use or freshly distilled from benzophenone ketyl. Methylene chloride was distilled over calcium hydride under a nitrogen atmosphere. Any other solvents were stored over 4-Å sieves for at least 48 h before use. Benzoyl chloride, acetyl chloride, and acetic anhydride were distilled prior to use. Triethylamine was refluxed over calcium hydride then distilled prior to use. All reactions were carried out under an argon or nitrogen atmosphere. Reactions which were heated or run over a longer period of time were carried out in a Pressure Flask which is a single necked flask equipped with a threaded high-vacuum stopcock that has previously been described.[12a] These reactions were deoxygenated by the freeze–thaw method (−196 °C to 25 °C, 3 times). Flash column chromatography was carried out as described by Still[20] using silica gel.

Melting points were determined in open capillary tubes using a Hoover melting point apparatus and are uncorrected. Routine proton NMR spectra were recorded on either a Bruker 270 MHz, General Electric QE-300 MHz or a DS 1000 (Chicago built) 500 MHz spectrometer in $CDCl_3$ (unless otherwise noted) with tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained with either a Varian XL-400 operating at 100 MHz or a General Electric QE-300 operating at 75 MHz. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer. Low-resolution mass spectra were recorded on a Finnigan 1015 instrument, and high resolution mass spectra were recorded on a VG 70-250 mass spectrometer. Elemental analyses were carried out by Galbraith Labs., Inc., Knoxville, TN.

Preparation of [(*O*-Methyl benzimidato)isopropylmethylene]pentacarbonylchromium (11). General Procedure for the Preparation of O-Alkyl Imidate Complexes from Nitrile Insertions. Phenylmethoxycarbene complex **2**[21] (500 mg, 1.60 mmol) was placed in a flame-dried Pressure Flask, and the flask was evacuated/filled with argon (3×). Benzene (10 mL) and isobutyronitrile (2.0 mL, 22.1 mmol) were added under argon. The dark red solution was deoxygenated by the freeze–thaw method and placed in an 80 °C oil bath for 24 h. After 24 h the solution was filtered through Celite and concentrated on a rotary evaporator. The crude residue was purified by flash chromatography using hexanes as eluent to give the starting material **2** as a red solid (44.7 mg, 0.143 mmol, 9%) and the insertion product **11** as an orange-yellow solid (443 mg, 1.16 mmol, 73%).

11: mp 43–44 °C; ^1H NMR ($CDCl_3$) δ 1.11 (d, 3 H), 1.20 (d, 3 H), 3.59 (m, 1 H), 3.87 (s, 3 H), 7.48 (m, 3 H), 7.63 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.90 (q, J_{C-H} = 124 Hz), 20.50 (q, J_{C-H} = 124 Hz), 50.99 (d, J_{C-H} = 135 Hz), 55.16 (q, J_{C-H} = 146 Hz), 126.38 (s), 127.46 (d, J_{C-H} = 157 Hz), 129.08 (d, J_{C-H} = 159 Hz), 132.11 (d, J_{C-H} = 159 Hz), 141.02 (s), 217.66 (s), 223.32 (s), 258.79 (s); IR ($CHCl_3$) 2054 m, 1970 w, 1934 s, 1807 m, 1305 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 381 M^+ (17), 353 (9), 297 (25), 269 (16), 241 (100), 226 (6), 211 (23), 198 (36), 172 (63), 158 (45), 129 (34), 105 (30), 77 (28), 68 (9). Anal. Calcd for $C_{17}H_{15}CrNO_6$: C, 53.54; H, 3.94. Found: C, 53.73; H, 4.10.

Preparation of [(*O*-Methyl benzimidato)methylmethylene]pentacarbonylchromium (4). The procedure described for complex **11** was followed, and to phenylmethoxycarbene complex **2** (249 mg, 0.797 mmol) was added benzene (5.4 mL) and acetonitrile (0.60 mL, 11.5 mmol). The starting material **2** was isolated as a red solid (93.9 mg, 0.301 mmol, 38%) and the insertion product **4** as a yellow solid (102 mg, 0.289 mmol, 36%).

4: mp 66–68 °C; ^1H NMR ($CDCl_3$) δ 2.87 (s, 3 H), 3.90 (s, 3 H), 7.47–7.59 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 37.49, 51.96, 123.09, 124.45, 125.61, 128.65, 134.23, 213.98, 219.96, 254.43; IR ($CHCl_3$) 2060 w, 1970 w, 1922 s, 1800 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 353 M^+ (25), 325 (9), 269 (10), 241 (34), 213 (74), 129 (66), 105 (27), 77 (28); calcd for $C_{15}H_{11}NO_6Cr$ *m/e* 352.9991, measd 352.995. Anal. (C, H, N were all found to be within 0.4% of calculated values).

Preparation of [(*O*-Methyl benzimidato)propylmethylene]pentacarbonylchromium (10). The procedure described for complex **11** was followed, and to phenylmethoxycarbene complex **2** (253 mg, 0.811 mmol) was added benzene (5 mL) and butyronitrile (1.0 mL, 11.5 mmol). The starting material **2** was isolated as a red solid (77.9 mg, 0.250 mmol, 31%) and the insertion product **10** as an orange-yellow solid (159 mg, 0.417 mmol, 51%).

10: mp 63–64 °C; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.51 (m, 2 H), 3.19 (t, 2 H), 3.88 (s, 3 H), 7.49 (m, 3 H), 7.58 (d, 2 H); ^{13}C

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(21) (a) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Fischer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (c) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 165.

NMR δ 13.52 (q), 20.44 (t), 55.34 (q), 55.95 (t), 126.59 (s), 127.77 (d), 129.12 (d), 132.13 (d), 138.59 (s), 217.63 (s), 223.36 (s), 257.38 (s); IR ($CHCl_3$) 2054 w, 1971 w, 1929 s, 1810 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 381 M^+ (12), 353 (5), 297 (18), 269 (7), 241 (64), 226 (7), 211 (13), 198 (44), 172 (100), 155 (28), 142 (16), 129 (43), 105 (26), 77 (24). Anal. Calcd for $C_{17}H_{15}CrNO_6$: C, 53.54; H, 3.94. Found C, 53.39; H, 4.00.

Preparation of [(*O*-Methyl benzimidato)*tert*-butylmethylene]pentacarbonylchromium (12). The procedure described for complex 11 was followed, and to phenylmethoxycarbene complex 2 (256 mg, 0.821 mmol) was added benzene (4.75 mL) and pivalonitrile (1.25 mL, 11.3 mmol). The starting material 2 was isolated as a red solid (86.8 mg, 0.278 mmol, 34%) and the insertion product 12 as a yellow solid (123 mg, 0.312 mmol, 38%).

12: mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 1.34 (s, 9 H), 3.90 (s, 3 H), 7.53 (m, 3 H), 7.60 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.12, 50.27, 55.18, 126.51, 127.34, 129.22, 132.07, 137.00, 218.21, 223.13, 257.41; IR ($CHCl_3$) 2052 m, 1967 w, 1921 s, 1919 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 395 M^+ (30), 343 (7), 311 (25), 283 (100), 255 (10), 188 (35), 172 (10), 131 (55), 98 (100); calcd for $C_{18}H_{17}O_6NCr$ *m/e* 395.04609, measd 395.04289. Anal. (C, H, N were all found to be within 0.4% of calculated values).

Preparation of [(*O*-Methyl benzimidato)benzylmethylene]pentacarbonylchromium (13). The procedure described for complex 11 was followed, and to phenylmethoxycarbene complex 2 (248 mg, 0.795 mmol) was added benzene (4.65 mL) and benzyl cyanide (1.35 mL, 11.2 mmol). The starting material 2 was isolated as a red solid (18.2 mg, 0.058 mmol, 7%) and the insertion product 13 as a yellow solid (244 mg, 0.568 mmol, 72%).

13: mp 70–72 °C; ^1H NMR ($CDCl_3$) δ 3.46 (s, 3 H), 4.43 (d, 1 H, *J* = 16.9 Hz), 4.56 (d, 1 H, *J* = 16.7 Hz), 6.94 (m, 2 H), 7.15 (m, 3 H), 7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 55.14, 59.86, 126.16, 127.25, 127.54, 128.62, 128.96, 129.10, 132.11, 135.36, 140.16, 217.59, 223.33, 252.22; IR ($CHCl_3$) 2060 w, 1970 w, 1925 s, 1810 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 429 M^+ (8), 401 (4), 345 (43), 289 (59), 274 (29), 259 (19), 246 (14), 117 (100), 90 (39), 77 (59); calcd for $C_{21}H_{15}NO_6Cr$ *m/e* 429.0304, measd 429.0304. Anal. (C, H, N were all found to be within 0.4% of calculated values).

Preparation of [(*O*-Methyl benzimidato)phenylmethylene]pentacarbonylchromium (14). The procedure described for complex 11 was followed, and to phenylmethoxycarbene complex 2 (253 mg, 0.809 mmol) was added benzene (4.85 mL) and benzonitrile (1.15 mL, 11.3 mmol). No starting material 2 remained. The insertion product 14 was isolated as an orange-red solid (285 mg, 0.686 mmol, 85%) after chromatography with a 1:1:20 mixture of ether/methylene chloride/hexanes as eluent.

14: mp 102.5–103.5 °C; ^1H NMR ($CDCl_3$) δ 4.01 (s, 3 H), 7.43–7.64 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 55.65, 126.11, 126.31, 128.19, 128.66, 129.17, 131.14, 132.25, 138.56, 145.48, 217.44, 223.96, 260.11; IR ($CHCl_3$) 2050 w, 1975 w, 1930 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 415 M^+ (2), 387 (2), 331 (2), 303 (6), 275 (15), 232 (25), 105 (20), 103 (56), 77 (20); calcd for $C_{20}H_{13}NO_6Cr$ *m/e* 415.01476, measd 415.01399. Anal. (C, H, N were all found to be within 0.4% of calculated values).

Preparation of [(*O*-Methyl benzimidato)*p*-anisylmethylene]pentacarbonylchromium (15). The procedure described for complex 11 was followed, and to phenylmethoxycarbene complex 2 (827 mg, 2.70 mmol) was added benzene (21 mL) and 4-methoxybenzonitrile (68.1 mg, 5.10 mmol). The insertion product 15 was isolated as a red solid (1.11 g, 2.48 mmol, 93%).

15: mp 103–104 °C; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 3.98 (s, 3 H), 6.93 (d, 2 H, *J* = 8.8 Hz), 7.43 (t, 2 H, *J* = 7.9 Hz), 7.48 (t, 1 H, *J* = 7.9 Hz), 7.56 (d, 2 H, *J* = 7.7 Hz), 7.69 (d, 2 H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 55.55, 59.51, 114.32, 126.68, 127.93, 128.33, 129.32, 130.56, 132.46, 137.30, 159.10, 218.05, 223.74, 253.15; IR ($CHCl_3$) 2055 w, 1970 w, 1920 s, 1760 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 445 M^+ (0.5), 418 (0.5), 361 (2.36); calcd for $C_{21}H_{15}NO_7Cr$ *m/e* 445.03044, measd 445.0253. Anal. (C, H, N were all found to be within 0.4% of calculated values).

Preparation of [(*O*-Methyl benzimidato)2-furylmethylene]pentacarbonylchromium (16). The procedure described for complex 11 was followed, and to phenylmethoxycarbene complex 2 (1.02 g, 3.25 mmol) was added benzene (20 mL) and 2-cyanofuran (1.0 mL, 11.4 mmol). The insertion product 16 was isolated as a red solid (1.21 g, 2.99 mmol, 92%).

16: mp 97.5–98 °C; ^1H NMR ($CDCl_3$) δ 3.97 (s, 3 H), 6.60 (dd, 1 H, *J* = 1.5 Hz, 3.3 Hz), 7.30 (d, 1 H, *J* = 3.5 Hz), 7.43 (t, 2 H, *J* = 7.9 Hz), 7.48 (t, 1 H, *J* = 7 Hz), 7.52 (d, 2 H, *J* = 7.3 Hz), 7.60 (d, 1 H, *J* = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 55.76, 114.27, 122.46, 127.12, 129.11, 129.18, 132.14, 137.99, 148.05, 155.13, 217.95, 224.29, 244.55; IR ($CHCl_3$) 2030 s, 1920 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 405 M^+ (24), 321 (40), 293 (15), 265 (84), 250 (16), 235 (52), 162 (100), 132 (83), 105 (29), 77 (36). Anal. Calcd for $C_{18}H_{11}O_7NCr$: C, 53.33; H, 2.72. Found: C, 52.99; H, 2.93.

Preparation of [(*O*-Methyl ethanimidato)phenylmethylene]pentacarbonylchromium (17). The procedure described for complex 11 was followed, and to methylmethoxycarbene complex 9[22] (266 mg, 1.06 mmol) was added benzene (11.6 mL) and benzonitrile (0.33 mL, 3.23 mmol). The insertion product 17 was isolated as an orange solid (254 mg, 0.718 mmol, 68%).

17: mp 39.5–41 °C; ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 3.75 (s, 3 H), 7.40 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.77, 55.39, 125.44, 128.50, 130.76, 133.67, 146.47, 217.51, 224.15, 261.26; IR (neat) 2040 w, 1895 s, 1810 w, 1260 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 353 M^+ (6), 325 (7), 241 (15), 213 (30), 172 (43), 170 (29), 142 (13), 129 (15), 103 (100), 80 (31), 52 (94); calcd for $C_{15}H_{11}O_6NCr$ *m/e* 352.9991, measd *m/e* 352.9965. Anal. Calcd for $C_{15}H_{11}O_6NCr$: C, 50.99; H, 3.12. Found: C, 50.68; H, 3.00.

Reaction of [(*O*-Methyl benzimidato)*tert*-butylmethylene]pentacarbonylchromium (12) with 1-Pentyne. Complex 12 (236 mg, 0.569 mmol) was dissolved in THF (7 mL) in a flame-dried Pressure Flask. 1-Pentyne (0.12 mL, 1.22 mmol) was added under argon flush. The solution was deoxygenated by the freeze–thaw method (4×) and heated in a 70 °C oil bath for 1 day. A solution of 0.5 M cerium ammonium nitrate (20 mL, 9.0 equiv) was added to the resulting crude brown mixture and the mixture stirred for one-half hour.[12a] The mixture was extracted with hexanes (3×), washed with brine (1×), and dried over $MgSO_4$. After concentration on a rotary evaporator a yellow oil remained. The yellow oil was purified by flash chromatography using 5% ethyl acetate/hexanes as eluent, and quinone 18 (46.2 mg, 0.231 mmol, 41%) was isolated. Quinone 18 was identified by comparing its spectral data to those of an authentic sample.[12a]

Equilibrium of (Phenylmethoxymethylene)pentacarbonylchromium (2), [(O-Methyl benzimidato)*tert*-butylmethylene]pentacarbonylchromium (12), and Pivalonitrile. Complex 12 (279 mg, 0.706 mmol) was dissolved in benzene (2 mL) and deoxygenated be the freeze–thaw method (3×). The solution was then heated for 36 h at 80 °C. Removal of the solvent and flash column chromatography of the residue gave phenylmethoxycarbene complex 2 (159 mg, 0.511 mmol) and insertion complex 12 (34.0 mg, 0.087 mmol). Thus the mole ratio of complex 2/complex 12 is 4.61/1, and the total mol % recovered is 85%.

Complex 2 (158 mg, 0.507 mmol) was heated with pivalonitrile (0.056 mL, 0.507 mmol) in benzene (1.43 mL) at 80 °C for 48 h to give complex 2 (118 mg, 0.378 mmol) and complex 12 (24.4 mg, 0.062 mmol). The mole ratio of complex 2/complex 12 is 4.84/1, and the total mol % recovered is 87%.

Preparation of [(*O*-Benzoyl benzimidato)*tert*-butylmethylene]pentacarbonylchromium (32). General Procedure for the Preparation of (*O*-Acyl imidato)carbene Complexes via Double Acylation. Method A. Ammonia was bubbled through an ether solution of (*tert*-butylmethoxymethylene) pentacarbonylchromium[23] to yield (amino-*tert*-butylmethylene)pentacarbonylchromium (26)[24] in greater than 90% yield after flash chromatography using a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent. The amino *tert*-butyl complex 26 (408 mg, 1.47 mmol) was placed in a flame-dried

(22) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. (b) Aumann, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 879. (c) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140. (d) Lam, C. T.; Malkiewich, C. D.; Senoff, C. V. *Inorg. Synth.* **1977**, *17*, 95.

(23) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

(24) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141.

round-bottom flask and dissolved in ether (25 mL). The yellow solution was cooled to 0 °C, and MeLi (1.1 mL, 1.54 mmol) was added. The pale yellow solution was stirred for 25 min, and benzoyl chloride (0.38 mL, 3.27 mmol) was added. The color of the solution darkened to orange upon addition of benzoyl chloride. The solution was stirred at 0 °C for 15 min and then warmed to room temperature and stirred for an additional 45 min. The orange solution was filtered through Celite and concentrated on a rotary evaporator. The resulting dark red oil was purified by flash chromatography using a mixture of 1:1:10 ether/methylene chloride/hexanes as eluent to give the imidate product **32** as a yellow solid (264 mg, 0.544 mmol, 37%) and the starting material **26** as a pale yellow solid (183 mg, 0.661 mmol, 45%). Crystals of **32** suitable for X-ray structure determination were grown from pentane solvent at 0 °C.

Method B. Amino *tert*-butyl complex **26** (58.5 mg, 0.211 mmol) prepared as described in method A above was placed in a flame-dried pressure flask, the flask was evacuated/filled with argon (3×), and methylene chloride (3 mL) was added. To this yellow solution were added benzoyl chloride (60 μL, 0.517 mmol) and triethylamine (0.25 mL, 1.79 mmol) under argon flow. There was a slight darkening in color upon addition of triethylamine. DMAP (2.0 mg, 0.016 mmol) was added, and the color of the solution became orange. The orange solution was deoxygenated by the freeze–thaw method (3×) and stirred at room temperature for 3 h. After 3 h the solution was filtered through Celite and concentrated on a rotary evaporator. The resulting orange solid was purified by flash chromatography using 1:1 benzene/hexanes as eluent to give the imidate product **32** as a yellow solid (94.9 mg, 0.196 mmol, 93%).

26: ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 8.53 (b s, 1 H), 8.77 (b s, 1 H).

32: mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 9 H), 7.50–7.59 (m, 7 H), 7.69 (t, 1 H), 8.18 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.13 (q, J_{C-H} = 127 Hz), 50.15 (s), 126.21 (s), 126.95 (d, J_{C-H} = 159 Hz), 127.53 (s), 129.06 (d, J_{C-H} = 152 Hz), 129.57 (d, J_{C-H} = 163 Hz), 130.21 (s)*, 130.55 (d, J_{C-H} = 162 Hz), 132.31 (d, J_{C-H} = 162 Hz), 134.86 (d, J_{C-H} = 162 Hz), 162.14 (s)*, 217.44 (s), 223.37 (s), 250.10 (s), peaks with an asterisk enhanced in ^{13}C-labeled compound (see ^{13}C data for **32a**); IR (neat) 2054 m, 1975 w, 1916 s, 1819 w, 1755 w, 1587 w, 1215 m, 1176 w, 1051 m, 1020 w, 704 w, 668 m, 653 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 485 M^+ (6), 345 (100), 317 (3), 276 (11), 262 (26), 234 (46), 220 (11), 178 (56), 135 (37), 105 (85), 89 (10), 77 (41), 68 (45). Anal. Calcd for $C_{24}H_{19}CrNO_7$: C, 59.38; H, 3.92%. Found: C, 59.89; H, 4.02.

Crystallographic Data for [(*O*-Benzoyl benzimidato)-*tert*-butylmethylene]pentacarbonylchromium (32). A pale yellow prismatic crystal of [(*O*-benzoyl benzimidato)*tert*-butylmethylene]pentacarbonylchromium (**32**) was transferred to a locally (Indiana University) modified Picker goniostat where it was cooled to −155 °C for characterization and data collection. Monoclinic symmetry with systematic absences of $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ allows the unambiguous assignment of the space group $P2_1/n$. Unit cell parameters are a = 13.268 (5) Å, b = 11.573 (4) Å, c = 15.951 (7) Å, β = 109.20 (2)°, and D_{calcd} = 1.394 g/cm^3 for Z = 4. A total of 3032 unique data were collected for $45° \geq 2\theta \geq 6°$ by using a moving crystal/moving detector technique. The structure was solved by direct methods and refined by full-matrix least squares using the 2416 data with $F > 2.33\sigma(F)$. Final residuals are $R(F)$ = 0.059 and $R_w(F)$ = 0.056.

Fractional coordinates are given in Table V below, and all other data are available in the supplementary material.

Preparation of ^{13}C-Labeled [(*O*-Benzoyl benzimidato)-*tert*-butylmethylene]pentacarbonylchromium (32a). Complex **32a** was prepared in the same manner as complex **32** following method A and using 99+ atom % ^{13}C benzoyl-*carbonyl*-^{13}*C* chloride obtained from Sigma-Aldrich.

32a: ^{13}C NMR ($CDCl_3$) δ 29.18 (s), 50.18 (d, J_{C-C} = 3.9 Hz), 126.21 (d, J_{C-C} = 77.3 Hz), 126.97 (d, J_{C-C} = 2.5 Hz), 127.56 (d, J_{C-C} = 77.5 Hz), 129.08 (d, J_{C-C} = 4.9 Hz), 129.59 (d, J_{C-C} = 5.4 Hz), 130.22 (d, J_{C-C} = 3.3 Hz, enhanced), 130.58 (d, J_{C-C} = 2.5 Hz), 132.31 (s), 134.88 (s), 162.17 (d, J_{C-C} = 3.6 Hz, enhanced), 217.45 (s), 223.38 (s), 250.20 (s); mass spectrum, *m/e* (% relative intensity) 487 M^+ (6), 459 (1), 375 (1), 347 (25), 279 (9), 264 (16), 235 (15), 220 (4), 207 (37), 191 (3), 180 (100), 166 (6), 153 (9), 144 (8), 129 (12), 119 (4), 106 (56), 91 (46), 77 (60), 68 (99).

Table V. Fractional Coordinates and Isotropic Thermal Parameters for 32 (MSC Sample No. 87836)[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Cr(1)	7097 (1)	1357 (1)	9841 (1)	15
C(2)	6012 (4)	2415 (5)	9859 (4)	19
O(3)	5365 (3)	3065 (4)	9864 (3)	31
C(4)	6446 (4)	138 (5)	10264 (3)	18
O(5)	6032 (3)	−653 (4)	10449 (3)	26
C(6)	7715 (4)	2458 (5)	9265 (4)	19
O(7)	8073 (3)	3100 (4)	8904 (3)	30
C(8)	8281 (5)	331 (5)	9973 (4)	22
O(9)	8969 (3)	−291 (4)	10070 (3)	36
C(10)	6286 (5)	825 (5)	8722 (4)	20
O(11)	5763 (3)	516 (3)	8033 (3)	25
C(12)	6755 (5)	1840 (7)	12005 (5)	25
C(13)	8379 (5)	569 (6)	12261 (5)	26
C(14)	8578 (5)	2627 (7)	12733 (4)	26
C(15)	7923 (4)	1783 (5)	12033 (4)	19
C(16)	7982 (4)	2064 (5)	11098 (3)	14
N(17)	8681 (3)	2822 (4)	11113 (3)	16
C(18)	9228 (4)	3700 (5)	11060 (3)	16
O(19)	10302 (3)	3643 (3)	11167 (2)	16
C(20)	10928 (4)	2695 (3)	11516 (4)	20
O(21)	10577 (3)	1782 (4)	11623 (3)	37
C(22)	12069 (4)	2980 (5)	11713 (3)	16
C(23)	12440 (5)	4105 (6)	11821 (4)	24
C(24)	13525 (4)	4339 (6)	12043 (5)	31
C(25)	14211 (5)	3430 (6)	12124 (5)	32
C(26)	13860 (5)	2305 (5)	12014 (4)	23
C(27)	12796 (4)	2081 (5)	11820 (4)	20
C(28)	8793 (4)	4861 (5)	10869 (3)	16
C(29)	9445 (5)	5810 (5)	10918 (4)	20
C(30)	9016 (5)	6903 (6)	10716 (4)	24
C(31)	7924 (5)	7061 (6)	10448 (4)	26
C(32)	7257 (5)	6125 (5)	10394 (4)	23
C(33)	7680 (5)	5041 (6)	10596 (4)	21
H(1)	649 (5)	262 (6)	1181 (4)	40 (10)
H(2)	632 (4)	129 (5)	1157 (4)	24 (10)
H(3)	675 (5)	159 (6)	1253 (5)	40 (10)
H(4)	838 (6)	35 (7)	1286 (6)	71 (10)
H(5)	801 (4)	−3 (5)	1188 (3)	8 (9)
H(6)	911 (5)	56 (5)	1227 (4)	26 (10)
H(7)	852 (3)	242 (4)	1327 (3)	0 (8)
H(8)	930 (6)	255 (6)	1283 (5)	53 (10)
H(9)	837 (4)	343 (5)	1258 (4)	24 (10)
H(10)	1201 (5)	466 (5)	1177 (4)	25 (10)
H(11)	1380 (5)	515 (6)	1214 (4)	38 (10)
H(12)	1484 (5)	359 (5)	1231 (4)	32 (10)
H(13)	1438 (4)	175 (5)	1207 (3)	17 (9)
H(14)	1254 (4)	138 (5)	1175 (3)	8 (9)
H(15)	1012 (6)	571 (7)	1106 (5)	65 (11)
H(16)	942 (5)	753 (5)	1080 (4)	30 (10)
H(17)	761 (5)	774 (5)	1029 (4)	27 (10)
H(18)	651 (6)	624 (6)	1018 (5)	60 (11)
H(19)	732 (4)	450 (5)	1063 (4)	15 (10)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Preparation of [(*O*-Acetyl ethanimidato)phenylmethylene]pentacarbonylchromium (23). Method A. The procedure described for complex **32** was followed and (aminophenylmethylene)pentacarbonylchromium (**21**)[25] (132 mg, 0.444 mmol) was dissolved in ether (1.8 mL). MeLi (0.32 mL, 0.448 mmol) and acetyl chloride (70 μL, 0.985 mmol) were added. The solution turned red upon addition of acetyl chloride. The solution was stirred for 30 min. Flash chromatography of the crude dark red oil using a mixture of 1:1:4 ether/methylene chloride/hexanes eluent gave the imidate product **23** as a bright red oil (84.0 mg, 0.147 mmol, 33%), the starting material **21** as a pale orange solid (61.6 mg, 0.207 mmol, 47%), and the monoacyl product **22** as a dark red semisolid (4.8 mg, 0.014 mmol, 3%).

23: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.38 (s, 3 H), 7.42 (m, 3 H), 7.55 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.46 (q, J_{C-H} = 131 Hz),

(25) Fischer, E. O.; Kollmeier, H-J. *Chem. Ber.* **1971**, *104*, 1339.

21.01 (q, J_{C-H} = 130 Hz), 127.47 (d, J_{C-H} = 159 Hz), 128.58 (d, J_{C-H} = 160 Hz), 130.01 (q, J_{C-H} = 7.1 Hz), 131.86 (d, J_{C-H} = 161 Hz), 142.23 (s), 166.32 (q, J_{C-H} = 6.9 Hz), 217.02 (s), 224.27 (s), 252.36 (s); IR (neat) 2057 s, 1978 s (sh), 1919 s, 1850 m, 1780 m, 1589 w, 1443 w, 1429 w, 1372 w, 1221 w, 1169 m, 1141 s, 1014 w, 878 w, 844 w, 657 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 381 M^+ (10), 297 (1), 269 (22), 253 (9), 241 (67), 220 (86), 200 (76), 175 (38), 155 (33), 141 (11), 129 (18), 108 (82), 89 (12), 80 (100).

Preparation of [(*O*-Benzoyl benzimidato)phenylmethylene]pentacarbonylchromium (29). Method A. The procedure described for complex **32** was followed, and (aminophenylmethylene)pentacarbonylchromium (**21**)[25] (302 mg, 1.02 mmol) was dissolved in ether (15 mL). MeLi (0.73 mL, 1.02 mmol) and benzoyl chloride (0.26 mL, 2.24 mmol) were added. The solution turned dark red upon addition of benzoyl chloride. The solution was stirred for 1 h. Flash chromatography of the crude dark red oil using a mixture of 1:1:10 ether/methylene chloride/hexanes eluent gave the imidate product **29** as a red solid (187 mg, 0.370 mmol, 36%) and starting material **21** as a pale orange solid (174 mg, 0.587 mmol, 58%).

Method B. The procedure described for complex **32** was followed, and aminophenyl complex **21**[25] (206 mg, 0.693 mmol) was dissolved in methylene chloride (10 mL). Benzoyl chloride (0.18 mL, 1.55 mmol) and triethylamine (0.80 mL, 5.74 mmol) were added. The orange solution turned dark red in color upon triethylamine addition. DMAP (5.0 mg, 0.041 mmol) was added. The reaction was stirred at room temperature for 15 min. Flash chromatography of the crude red solid in 1:1 benzene/hexanes gave the imidate product **29** as a red solid (338 mg, 0.669 mmol, 97%).

29: mp 126–128 °C dec; ^1H NMR ($CDCl_3$) δ 7.47 (m, 3 H), 7.52 (m, 5 H), 7.63 (d, 2 H), 7.69 (t, 1 H), 7.78 (m, 2 H), 8.20 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 126.18 (s), 127.52 (s), 127.86 (d, J_{C-H} = 162 Hz), 128.32 (d, J_{C-H} = 163 Hz), 128.72 (d, J_{C-H} = 164 Hz), 128.98 (d, J_{C-H} = 162 Hz), 129.47 (d, J_{C-H} = 165 Hz), 129.86 (s), 130.53 (d, J_{C-H} = 158 Hz), 132.20 (d, J_{C-H} = 161 Hz), 132.52 (d, J_{C-H} = 161 Hz), 134.78 (d, J_{C-H} = 161 Hz), 141.16 (s), 162.20 (s), 216.87 (s), 224.22 (s), 252.12 (s); ^{13}C NMR (acetone-d_6) δ 126.67 (s), 128.37 (s), 128.75 (d, J_{C-H} = 163 Hz), 128.86 (d, J_{C-H} = 166 Hz), 129.65 (d, J_{C-H} = 160 Hz), 129.96 (d, J_{C-H} = 163 Hz), 130.50 (d, J_{C-H} = 168 Hz), 131.17 (s), 131.24 (d, J_{C-H} = 159 Hz), 133.13 (d, J_{C-H} = 161 Hz), 133.72 (d, J_{C-H} = 163 Hz), 135.78 (d, J_{C-H} = 162 Hz), 142.32 (s), 162.82 (s), 217.67 (s), 224.88 (s), 249.91 (s); IR (neat) 2056 s, 1981 m, 1919 s, 1804 m, 1750 m, 1599 w, 1451 w, 1314 w, 1261 w, 1217 s, 1175 m, 1159 m, 1074 w, 1046 m, 1019 m, 1002 w, 836 w, 764 w, 704 m, 690 w, 662 s, 617 w cm^{-1}, mass spectrum, *m/e* (% relative intensity) 505 M^+ (3), 365 (5), 297 (97), 269 (16), 220 (67), 192 (6), 165 (100), 149 (5), 136 (7), 108 (79), 89 (25), 80 (94), 77 (30), 68 (4). Anal. Calcd for $C_{26}H_{15}CrNO_7$: C, 61.78; H, 2.97; N, 2.77. Found: C, 61.92; H, 3.21; N, 2.75.

Preparation of [(*O*-Acetyl ethanimidato)methylmethylene]pentacarbonylchromium (30). Method A. The procedure described for complex **32** was followed, and (aminomethylmethylene)pentacarbonylchromium (**24**)[24] (215 mg, 0.916 mmol) was dissolved in ether (20 mL). MeLi (0.66 mL, 0.924 mmol) and acetyl chloride (0.15 mL, 2.11 mmol) were added. The color of the solution darkened to orange upon addition of acetyl chloride. The solution was stirred for 1 h. Flash chromatography of the crude yellow-orange solid using a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent gave the imidate product **30** as a yellow oil (55.5 mg, 0.174 mmol, 19%) and starting material **24** as a pale yellow solid (151 mg, 0.642 mmol, 70%).

Method B. The procedure described for complex **32** was followed, and amino methyl complex **24**[24] (110 mg, 0.469 mmol) was dissolved in methylene chloride (10 mL). Acetic anhydride (0.10 mL, 1.06 mmol) and triethylamine (0.35 mL, 2.51 mmol) were added. The yellow solution turned orange and then brown in color after triethylamine addition. DMAP (27.6 mg, 0.226 mmol) was added. The reaction was stirred at room temperature for 2 h. The resulting brownish yellow solid was purified by flash chromatography using a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent. Only the DMAP complex **37** was isolated (53.5 mg, 0.170 mmol, 36% based on **24**).

30: ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H), 2.29 (s, 3 H), 2.73 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 19.03, 21.06, 38.33, 129.09, 165.99, 217.00, 223.73, 253.42; IR (neat) 2860 w, 2058 m, 1911 s, 1778 m, 1435 w, 1340 w, 1142 m, 1007 w, 651 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 319 M^+ (11), 263 (2), 223 (21), 207 (12), 191 (5), 179 (10), 167 (10), 149 (100), 135 (8), 121 (6), 111 (22), 108 (16), 93 (17), 83 (16), 69 (27).

37: ^1H NMR ($CDCl_3$) δ 2.99 (s, 6 H), 6.32 (d, 2 H), 7.97 (d, 2 H); IR (neat) 1917 s, 806 w, 658 w, 646 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 314 M^+ (5), 286 (3), 258 (3), 244 (5), 230 (3), 202 (9), 174 (20), 121 (100), 105 (10), 94 (12), 78 (20), 66 (3).

Preparation of [(*O*-Benzoyl benzimidato)isopropylmethylene]pentacarbonylchromium (31). Method A. The procedure described for complex **32** was followed, and (aminoisopropylmethylene)pentacarbonylchromium (**25**) (261 mg, 0.994 mmol), prepared by two sequential alkylations of methylmethoxycarbene complex using methyl triflate,[26] was dissolved in ether (15 mL). MeLi (0.71 mL, 0.994 mmol) and benzoyl chloride (0.25 mL, 2.15 mmol) were added. The solution darkened to an orange color upon addition of benzoyl chloride. The solution was stirred for 1 h. Flash chromatography using a mixture of 1:1:10 ether/methylene chloride/hexanes as eluent gave the imidate product **31** as an orange-yellow solid (239 mg, 0.507 mmol, 51%) and the starting material **25** as a pale yellow solid (126 mg, 0.480 mmol, 48%).

25: ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.17 (s, 3 H), 3.45 (heptet, 1 H), 8.38 (b s, 1 H), 8.61 (b s, 1 H).

31: mp 64–65 °C; ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H), 1.27 (d, 3 H),3.60 (heptet, 1 H), 7.55 (m, 5 H), 7.61 (d, 2 H), 7.69 (t, 1 H), 8.17 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.32, 20.37, 50.66, 125.80, 126.23, 127.12, 127.49, 129.05, 129.51, 130.57, 132.40, 134.83, 162.31, 216.98, 223.66, 252.65; IR (neat) 2056 m, 1978 w, 1919 s, 1809 w, 1753 w, 1589 w, 1449 w, 1214 m, 1045 m, 1019 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 471 M^+ (12), 359 (5), 331 (100), 276 (17), 262 (27), 234 (45), 219 (6), 198 (6), 169 (16), 155 (5), 129 (31), 105 (61), 69 (58). Anal. Calcd for $C_{23}H_{17}O_7NCr$: C, 58.60; H, 3.61; N, 2.97. Found: C, 58.82; H, 3.69; N, 2.70.

Preparation of [(*O*-*p*-Chlorobenzoyl *p*-chlorobenzimidato)*tert*-butylmethylene]pentacarbonylchromium (33). Method B. The procedure described for complex **32** was followed, and amino *tert*-butyl complex **26** (48.0 mg, 0.173 mmol) was dissolved in methylene chloride (2.5 mL). *p*-Chlorobenzoyl chloride (50 μL, 0.393 mmol) and triethylamine (0.20 mL, 1.44 mmol) were added. The yellow solution became slightly darker in color after triethylamine addition. DMAP (4.4 mg, 0.036 mmol) was added. The color of the solution became orange upon DMAP addition. The reaction was stirred at room temperature for 3 h. Flash chromatography in 1:3 benzene/hexanes gave the imidate product **33** as an orange solid (85.6 mg, 0.155 mmol, 89%).

33: mp 135–140 °C dec; ^1H NMR ($CDCl_3$) δ 1.39 (s, 9 H), 7.50 (s, 4 H), 7.54 (d, 2 H), 8.11 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.17, 50.35, 124.73, 125.70, 128.01, 129.47, 129.54, 130.04, 131.85, 138.91, 141.82, 161.31, 217.26, 223.11, 252.44; ^{13}C NMR (acetone-d_6) δ 28.97, 50.82, 125.52, 126.92, 129.53, 129.97, 130.18, 130.71, 132.87, 139.19, 141.72, 161.98, 217.98, 223.86, 250.11; IR (neat) 2054 m, 1981 w, 1915 s, 1815 w, 1756 w, 1601 w, 1213 w, 1051 w, 1008 w, 667 m, 651 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 554 M^+ (3, ^{37}Cl), 552 M^+ (4, ^{35}Cl), 451 (1), 438 (2), 415 (8, ^{37}Cl), 413 (13, ^{35}Cl), 347 (3, ^{37}Cl), 345 (5, ^{35}Cl), 332 (5, ^{37}Cl), 330 (8, ^{35}Cl), 304 (2, ^{37}Cl), 302 (3, ^{35}Cl), 248 (58, ^{37}Cl), 246 (87, ^{35}Cl), 220 (13), 207 (4), 192 (4), 178 (12, ^{37}Cl), 176 (26, ^{35}Cl), 152 (59), 139 (66), 124 (42), 111 (26), 89 (64), 80 (27), 68 (100); Anal. Calcd for $C_{24}H_{17}Cl_2CrNO_7$: C, 51.99; H, 3.07; N, 2.53. Found: C, 52.06; H, 3.32; N, 2.32.

Preparation of [(*O*-*p*-Anisoyl *p*-anisimidato)*tert*-butylmethylene]pentacarbonylchromium (34). Method A. The procedure described for complex **32** was followed, and (amino-*tert*-butylmethylene)pentacarbonylchromium (**26**) (250 mg, 0.901 mmol) was dissolved in ether (15 mL). MeLi (0.65 mL, 0.910 mmol) and *p*-anisoyl chloride (334 mg, 1.96 mmol) were added. The solution was stirred for 1 h and became brownish orange in color. Flash chromatography of the crude dark red oil using a mixture of 1:1:10 ether/methylene chloride/hexanes as eluent gave the imidate product **34** as a yellow solid (202 mg, 0.371 mmol,

(26) Anderson, B. A.; Wulff, W. D., unpublished results.

41%) and starting material **26** as a pale yellow solid (155 mg, 0.560 mmol, 62%).

Method B. The procedure described for complex **32** was followed, and amino *tert*-butyl complex **26** (56.9 mg, 0.205 mmol) was dissolved in methylene chloride (3 mL). *p*-Anisoyl chloride (60 μL, 0.444 mmol) and triethylamine (0.25 mL, 1.79 mmol) were added. There was a slight darkening of color. DMAP (2.0 mg, 0.016 mmol) was added. The color of the solution became orange. The reaction was stirred at room temperature for 3 days. Flash chromatography in a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent gave the imidate product **34** as a yellow solid (86.0 mg, 0.158 mmol, 77%) and the starting complex **26** as a pale yellow solid (10.1 mg, 0.036 mmol, 18%).

34: mp 92–94 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 3.85 (s, 3 H), 3.90 (s, 3 H), 7.00 (m, 4 H), 7.50 (d, 2 H), 8.12 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.02 (q, J_{C-H} = 127 Hz), 50.09 (q, J_{C-H} = 3.6 Hz), 55.49 (q, J_{C-H} = 144 Hz), 55.55 (q, J_{C-H} = 144 Hz), 114.28 (d, J_{C-H} = 161 Hz), 115.10 (d, J_{C-H} = 127 Hz), 117.78 (s), 119.61 (s), 128.77 (d, J_{C-H} = 160 Hz), 130.67 (s), 132.73 (d, J_{C-H} = 163 Hz), 161.74 (s), 162.91 (s), 164.81 (s), 217.57 (s), 223.43 (s), 250.05 (s); IR (neat) 2967 w, 2937 w, 2054 m, 1974 m, 1911 s, 1829 m, 1747 m, 1605 m, 1513 m, 1461 w, 1367 w, 1310 w, 1264 m, 1226 m, 1164 m, 1056 m, 1028 m, 1002 w, 834 w, 759 w, 670 m, 655 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 545 M$^+$ (3), 405 (8), 337 (11), 322 (7), 275 (4), 238 (100), 223 (71), 195 (15), 173 (24), 152 (15), 135 (30), 119 (12), 103 (6), 90 (7), 80 (16), 68 (74); Anal. Calcd for $C_{26}H_{23}CrNO_9$: C, 57.25; H, 4.22; N, 2.57. Found: C, 57.30; H, 4.33; N, 2.43.

Preparation of [(*O*-Acetyl ethanimidato)*tert*-butylmethylene]pentacarbonylchromium (35). Method A. The procedure described for complex **32** was followed and (amino-*tert*-butylmethylene)pentacarbonylchromium (**26**) (134 mg, 0.484 mmol) was dissolved in ether (10 mL). MeLi (0.35 mL, 0.490 mmol) and acetyl chloride (90 μL, 1.27 mmol) were added. The solution darkened to an orange-brown color upon addition of acetyl chloride. The solution was stirred for 2 h. Flash chromatography using a mixture of 1:1:10 ether/methylene chloride/hexanes as eluent gave the imidate product **35** as a bright yellow oil (48.9 mg, 0.135 mmol, 28%) and starting material **26** as a pale yellow solid (69.0 mg, 0.249 mmol, 52%).

Method B. The procedure described for complex **32** was followed and amino *tert*-butyl complex **26** (39.7 mg, 0.143 mmol) was dissolved in methylene chloride (4 mL). Acetic anhydride (70 μL, 0.742 mmol) and triethylamine (0.15 mL, 1.08 mmol) were added. DMAP (1.1 mg, 0.009 mmol) was added. There was a slight darkening in the color of the reaction. The reaction was stirred at room temperature for 3 days. The color of the solution became orange after 1 day. Flash chromatography using a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent gave the imidate product **35** as a bright yellow oil (8.7 mg, 0.024 mmol, 17%), the DMAP complex as a yellow solid (3.6 mg, 0.012 mmol, 8% based on **26**), and the starting complex **26** as a pale yellow solid (23.3 mg, 0.084 mmol, 59%).

35: ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 2.23 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.91, 20.97, 28.67, 48.65, 129.55, 166.24, 217.57, 223.28, 249.33; IR (neat) 2056 m, 1974 w (sh), 1911 s, 1858 m (sh), 1783 w, 1459 w, 1369 w, 1146 m, 1015 w, 890 w, 863 w, 669 m, 653 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 361 M$^+$ (5), 305 (2), 282 (2), 249 (12), 233 (10), 221 (16), 206 (4), 194 (84), 180 (9), 165 (38), 152 (22), 135 (26), 120 (3), 111 (56), 93 (7), 79 (31), 68 (100); Anal. Calcd for $C_{14}H_{15}CrNO_7$: C, 46.54%; H, 4.16; N, 3.88. Found: C, 46.53; H, 4.25; N, 3.81.

Preparation of [(*O*-Acetyl ethanimidato)4-hexynylmethylene]pentacarbonylchromium (36). Method A. (4-Hexynylmethoxymethylene)pentacarbonylchromium (**28**) was obtained through the triflate alkylation of methylmethoxycarbene complex **9**[22] developed in our labs.[18] Amino-4-hexynylcarbene complex **27** was obtained by bubbling ammonia through the 4-hexynylmethoxycarbene complex[24] **28** in a 60% overall yield starting from methylmethoxycarbene complex **9**. Amino-4-hexynyl complex **27** (954 mg, 3.17 mmol) was then dissolved in ether (20 mL) as described for complex **32**. MeLi (2.26 mL, 3.16 mmol) and acetyl chloride (0.50 mL, 7.03 mmol) were added. The solution was stirred for 1 h and became a brown-orange in color. Flash chromatography using a mixture of 1:1:4 ether/methylene chloride/hexanes as eluent gave the imidate product **36** as a brownish orange oil (508 mg, 1.32 mmol, 42%) and the starting material **27** as a yellow oil (372 mg, 1.23 mmol, 39%).

27: ^{1}H NMR ($CDCl_3$) δ 1.78 (t, 3 H), 1.84 (pentet, 2 H), 2.19 (m, 2 H), 3.09 (t, 2 H), 8.50 (b s, 1 H), 8.60 (b s, 1 H).

36: ^{1}H NMR ($CDCl_3$) δ 1.69 (m, 2 H), 1.77 (t, 3 H), 2.15 (m, 2 H), 2.23 (s, 3 H), 2.31 (s, 3 H), 3.12 (m, 1 H), 3.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 3.37 (q, J_{C-H} = 130 Hz), 17.98 (t, J_{C-H} = 131 Hz), 18.91 (q, J_{C-H} = 132 Hz), 20.97 (q, J_{C-H} = 130 Hz), 25.68 (t, J_{C-H} = 130 Hz), 50.03 (t, J_{C-H} = 130 Hz), 76.95 (s), 77.45 (s), 130.85 (q, J_{C-H} = 7.3 Hz), 166.08 (q, J_{C-H} = 7.2 Hz), 217.02 (s), 223.63 (s), 250.48 (s); IR (neat) 2057 m, 1977 m, 1917 s, 1856 m (sh), 1780 w, 1436 w, 1371 w, 1145 m, 1009 w, 655 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 385 M$^+$ (16), 245 (86), 230 (27), 217 (6), 202 (22), 185 (38), 173 (36), 158 (23), 144 (53), 132 (20), 111 (100), 91 (52), 80 (27), 67 (19).

Preparation of [(*N*-Acetylamino)phenylmethylene]pentacarbonylchromium (22) via Method B. (Aminophenylmethylene)pentacarbonylchromium (**21**)[25] (301 mg, 1.01 mmol) was placed in a flame-dried round-bottom flask and dissolved in methylene chloride (15 mL). To this yellow solution were added acetyl chloride (0.16 mL, 2.25 mmol) and triethylamine (1.3 mL, 9.33 mmol). Immediately upon addition of triethylamine the color of the solution turned a dark red. DMAP (10.5 mg, 0.086 mmol) was added, and the solution was stirred at room temperature for 14 h. The solution was filtered through Celite and concentrated on a rotary evaporator. The resulting dark red semisolid was purified by flash chromatography using 1:1:4 ether/methylene chloride/hexanes as eluent to give the DMAP complex **37** as a yellow solid (37.1 mg, 0.118 mmol, 12% based on complex **21**) and the starting material **21** as a pale orange solid (57.2 mg, 0.193 mmol, 19%). The eluent was switched to 1:1:1 ether/methylene chloride/hexanes to give the very polar mono-acyl product **22** as a dark red semisolid (91.3 mg, 0.269 mmol, 27%).

Optimal Procedure for the Preparation of [(*N*-Acetylamino)phenylmethylene]pentacarbonylchromium (22). (Aminophenylmethylene)pentacarbonylchromium (**21**)[25] (107 mg, 0.361 mmol) was placed in a flame-dried round-bottom flask and dissolved in methylene chloride (10 mL). To this yellow solution were added acetic anhydride (40 μL, 0.424 mmol) and triethylamine (60 μL, 0.430 mmol). There was a slight darkening of color upon addition of triethylamine. DMAP (5.5 mg, 0.045 mmol) was added, and the solution became orange. Within 15 min of stirring at room temperature, the color of the solution was dark red. The solution was stirred at room temperature for a total of 25 min, filtered through Celite, and concentrated on a rotary evaporator. The resulting dark red oil was purified by flash chromatography using 30% ethyl acetate/hexanes as eluent to give the starting material **21** as a pale orange solid (12.1 mg, 0.041 mmol, 11%), and the mono-acyl product **22** as a dark red semisolid (106 mg, 0.312 mmol, 86%). The yield of mono-acyl product **22** is typically between 80 and 86%.

22: ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 7.50 (s, 3 H), 7.66 (d, 2 H), 10.17 (b s, 1 H); ^{13}C NMR (acetone-d_6) δ 21.34, 126.78, 129.18, 132.29, 147.61, 183.86, 205.70, 212.51, 317.54; IR (neat) 3240 bw, 2015 m, 1950 s (sh), 1915 s, 1852 m, 1644 w, 1593 w, 1551 w, 1474 w, 1438 w, 1235 w, 1136 w, 658 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 311 (M$^+$ − 28) (1), 283 (1), 255 (1), 237 (3), 227 (2), 220 (4), 205 (5), 199 (4), 187 (3), 179 (3), 171 (2), 163 (26), 149 (5), 144 (3), 135 (5), 121 (44), 105 (100), 97 (3), 91 (6), 77 (93), 71 (4), 65 (4). Anal. Calcd for $C_{14}H_9CrNO_6$: C, 49.57; H, 2.67; N, 4.13. Found: C, 50.40; H, 3.03; N, 4.12.

Methylation of [(*O*-Methyl benzimidato)benzylmethylene]pentacarbonylchromium (13) To Give Diastereomers 38a and 38b. Complex **13** (301 mg, 0.701 mmol) was dissolved in THF (10 mL) and cooled to −78 °C. *n*-BuLi (0.44 mL, 0.701 mmol) was added dropwise to this solution over 2 min. Upon being warmed to 0 °C and stirred for 5 minutes, the yellow solution turned orange then dark red. After being stirred for 20 min at 0 °C, the mixture was cooled to −78 °C and methyl triflate (0.10 mL, 0.884 mmol) was added dropwise. The solution became yellow once again. The reaction was warmed to 0 °C and stirred for 30 min. The reaction was diluted with ether (30 mL) and quenched with pH 7 buffer (15 mL). The solution was washed with brine, dried over sodium sulfate, and concentrated on a rotary evaporator. Crude ^{1}H NMR of the resulting yellow oil showed

a 14:1 ratio of diastereomers **38a** to **38b**. The diastereomers were separated by preparative TLC (silica gel) using 1:50 ethyl acetate/hexanes as eluent in a 9:1 ratio. The minor isomer **38b** was obtained as a yellow oil (23.3 mg, 0.053 mmol, 8%). The major isomer **38a** was obtained as a yellow solid (203 mg, 0.457 mmol, 65%) which was crystalized from hexanes at 0 °C to give crystals suitable for X-ray structure determination. The total yield of diastereomers was 73%.

Each of the two pure diastereomers **38a** (19.9 mg, 0.044 mmol) and **38b** (21.4 mg, 0.048 mmol) were placed in a NMR tube and dissolved in $CDCl_3$. The solutions were deoxygenated by the freeze–thaw method (3×) and sealed under vacuum. Each of the two tubes was monitored by NMR daily, and after 10 days at room temperature each diastereomer epimerized to give a 1:1.65 ratio in favor of the minor isomer **38b**. After the 10 days the tubes were opened and TLC showed only the two diastereomer spots present. Thus no side products could be detected by TLC, and no side reactions had apparently occurred. After chromatography of the solution in each tube, the mass recovery of the 1:1.65 mixture of **38a** and **38b** starting from **38a** was 62% (12.0 mg, 0.027 mmol) and starting from **28b** the mass recovery was 77% (16.3 mg, 0.037 mmol).

38a: mp 71–72 °C; ^{1}H NMR ($CDCl_3$) δ 1.59 (d, 3 H), 3.94 (s, 3 H), 4.87 (q, 1 H), 7.10 (m, 3 H), 7.21 (m, 5 H), 7.37 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.16 (q), 55.28 (q), 61.61 (d), 125.72 (d), 127.26 (d), 127.52 (d), 128.49 (d), 128.68 (d), 131.88 (d), 132.19 (s), 139.20 (s), 139.30 (s), 217.48 (s), 223.14 (s), 256.78 (s); IR ($CHCl_3$) 2927 w, 2053 w, 1977 w, 1929 s, 1795 w, 1262 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 443 M^+ (4), 415 (2), 359 (18), 303 (23), 288 (6), 199 (13), 172 (17), 155 (7), 131 (41), 116 (100), 103 (21), 89 (13), 77 (24). Anal. Calcd for $C_{22}H_{17}O_6NCr$: C, 59.59; H, 3.84. Found: C, 59.65; H, 4.05.

38b: ^{1}H NMR ($CDCl_3$) δ 1.59 (d, 3 H), 3.03 (s, 3 H), 4.87 (q, 1 H), 7.12 (d, 2 H), 7.25 (m, 3 H), 7.50 (m, 3 H), 7.66 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.30 (q), 54.81 (q), 62.49 (d), 126.47 (d), 127.36 (d), 127.39 (d), 127.48 (d), 128.53 (d), 129.19 (d), 131.93 (s), 132.25 (s), 140.35 (s), 217.61 (s), 223.17 (s), 253.27 (s); IR ($CHCl_3$) 2937 w, 2054 w, 1978 w, 1929 s, 1801 w, 1248 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 443 M^+ (4), 415 (2), 359 (16), 303 (21), 288 (5), 199 (12), 172 (18), 155 (6), 131 (39), 116 (100), 103 (15), 89 (13), 77 (20).

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Supplementary Material Available: X-ray crystallographic data for compound **32** including a VERSORT and tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (9 pages); a listing of F_o and F_c (7 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of the Cationic Thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$. Reactions of the Thiocarbene $[HC(pz)_3](CO)_2W[\eta^2\text{-}CHSMe]^{2+}$ with Nucleophiles

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The thiocarbonyl complex $[HC(pz)_3](CO)_2W(CS)$ (**1**) is prepared by reaction of *trans*-$IW(CO)_4(CS)^-$ with $HC(pz)_3$, tris(1-pyrazolyl)methane. The nucleophilic sulfur atom of the CS ligand is methylated with Me_3O^+ to give the thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (**2**). Reaction of the carbyne (**2**) with phosphorus nucleophiles (PR_3) gives the η^2-ketenyl derivatives $[HC(pz)_3](CO)(PR_3)W[C(O)CSMe]^+$. Methylation of $[HC(pz)_3](CO)(PMe_3)W[C(O)CSMe]^+$ at the ketenyl oxygen atom yields the acetylene complex $[HC(pz)_3](CO)(PMe_3)W(MeOC{\equiv}CSMe)^{2+}$. The title thiocarbene complex $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^{2+}$ (**3**) is prepared by protonation of the carbyne carbon atom in $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ with $HBF_4{\cdot}Et_2O$. Reactions of **3** with PR_3, SR^-, and $NaBH_4$ nucleophiles give the carbene adducts $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(L)SMe]^+$. These studies show that the reactivity of the cationic $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (**2**) is similar to that of electron-rich carbynes like $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ rather than to the reactivity of cationic Fischer carbynes.

Introduction

In recent years, the preparations and reactions of thiocarbene[1] and thiocarbyne[2] complexes have been studied extensively in this laboratory. The thiocarbyne complex $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$,[3] where $HB(pz)_3^-$ is the hydrotris(1-pyrazolyl)borato ligand, is similar in its reactivity to other electron-rich carbynes.[4] Thus, treating the

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