Reaction of Fischer Type Chromium Carbene Complexes with *N,N*-Dimethylformamide Dialkyl Acetals (DMF-DAA): An Unexpected Carbon-Carbon Bond Breaking

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A series of pentacarbonyl(2-oxacyclopentylidene)chromium (**5a-f**) were reacted with *N,N*-dimethylformamide dimethyl acetal (DMF-DMA), resulting in the pentacarbonyl(2-oxa-5-[(*N,N*-dimethylamino)methylidene]cyclopentylidene)chromium (**6a-f**) and the unexpected pentacarbonyl(2-oxa-5-(cyclopropylmethylidene)cyclopentylidene)chromium (**7a-d**). Open chain Fischer type carbene complexes $(CO)_5Cr{=}C(OCH_3)CH_2R_1$ (**1a-d**) also react easily with DMF-DAA (**2a-d**). When R_1 = H, the carbene complex $(CO)_5Cr{=}C(OCH_3)CH{=}CHN(CH_3)_2$ is formed in high yield; however, when R_1 = alkyl, the reaction products are dialkoxy complexes $(CO)_5Cr{=}C(OCH_3)OR_2$ (**4a-d**), in which the OR_2 group comes from the DMF-DAA. The mechanisms of the above reactions are elucidated. The cyclopropyl ring present on compounds **7a-d** arises from a contraction of the five membered ring of complexes **5a-d** due to the breaking of the bond between the carbene carbon atom and the α-carbon atom. The same mechanism explains the formation of dialkoxy complexes **4a-d** from complexes **1b-d**. In the case of the reaction of the complex $(CO)_5Cr{=}C(OCH_3)CH_2CH_2CH_2CH_3$ (**1d**) with *N,N*-dimethylformamide dineopentyl acetal (**2d**), the intermediary formation of an enamine derivative has been demonstrated. Moreover the reaction of pentacarbonyl(2-oxa-4,4-dimethylcyclopentylidene)-chromium (**5g**) with DMF-DMA (**2a**) allowed the isolation of 2,2-dimethylcyclopropanecarbaldehyde (characterized as the (2,4-dinitrophenyl)hydrazone).

Introduction

Fischer type carbene complexes are useful reagents in many areas of organic synthesis.[1,2] The high thermodynamic acidity of hydrogens on the carbon bound to the carbene carbon atom[3] is one of their peculiar features which has been exploited in order to introduce new functionalities by means of reactions with electrophilic reagents.[4,5] We have already reported the transformation of chromium carbene complexes **1a** and **5b** by means of their reaction with *N,N*-dimethylformamide dimethyl acetal **2a** (DMF-DMA) under mild experimental conditions into their corresponding enamine derivatives **3a** and **6b** in very good yields.[6] However, the same reaction performed on complexes **1b-d** always led to the production of pentacarbonyl-(dimethoxycarbene)chromium (**4a**) (Scheme I). Moreover, the reaction of **1d** with *N,N*-dimethylformamide dialkyl acetals (DMF-DAA, **2b-d**) produced pentacarbonyl-(dialkoxycarbene)chromium derivatives **4b-d**, in which the OR_2 group is the one present in the starting DMF-DAA.[6]

The present report provides full details of the synthesis of the above complexes and their reactions with DMF-DAA. It also describes some new and unexpected results when the reaction with DMF-DMA was extended to the pentacarbonyl(2-oxacyclopentylidene)chromium complexes **5a,c-g**. In addition, experiments are presented which bear on the mechanism of the above reactions. The full results have allowed us to draw an almost complete picture of the reactivity of carbene complexes **1** and **5** with *N,N*-dimethylformamide dialkyl acetals.

Results and Discussion

Complexes **5a-f** were synthesized following our previously reported procedure.[5] In all cases, the reactions of **5a,c-f** with DMF-DMA occurred very smoothly at room temperature and gave the new carbene complexes **6a,c-f** (Scheme II).[7] However, in the case of complexes **5a,c,d** we also observed the formation of variable amounts of (cyclopropylcarbene)chromium complexes **7a,c,d**, the yield

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(2) Miller, J. R.; Pulley, S. R.; Hegedus, L. S.; DeLombaert, S. *J. Am. Chem. Soc.* **1992**, *114*, 5602. Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985. Grotjahn, D. B.; Kroll, F. E. K.; Schäfer, T.; Harms, K.; Dötz, K. H. *Organometallics* **1992**, *11*, 298.

(3) Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282 and references cited therein.

(4) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263. Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28. Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175. Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *Advances in Metal Carbene Complexes*; Nato ASI Series C 269; Kluwer: Dordrecht, The Netherlands, 1989; p 149. Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437. Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti-Gerosa, A. *Synlett* **1992**, 315.

(5) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807.

(6) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A.; Chiesi-Villa, A.; Guastini, G. *J. Chem. Soc., Chem. Commun.* **1988**, 1092.

(7) It is noteworthy that the reaction of γ-butyrolactone with the very reactive tris(dimethylamino)methane gives the corresponding enaminolactone after 48 h at 75 °C.[8]

(8) Martin, S. F.; Moore, D. R. *Tetrahedron Lett.* **1976**, 4459.

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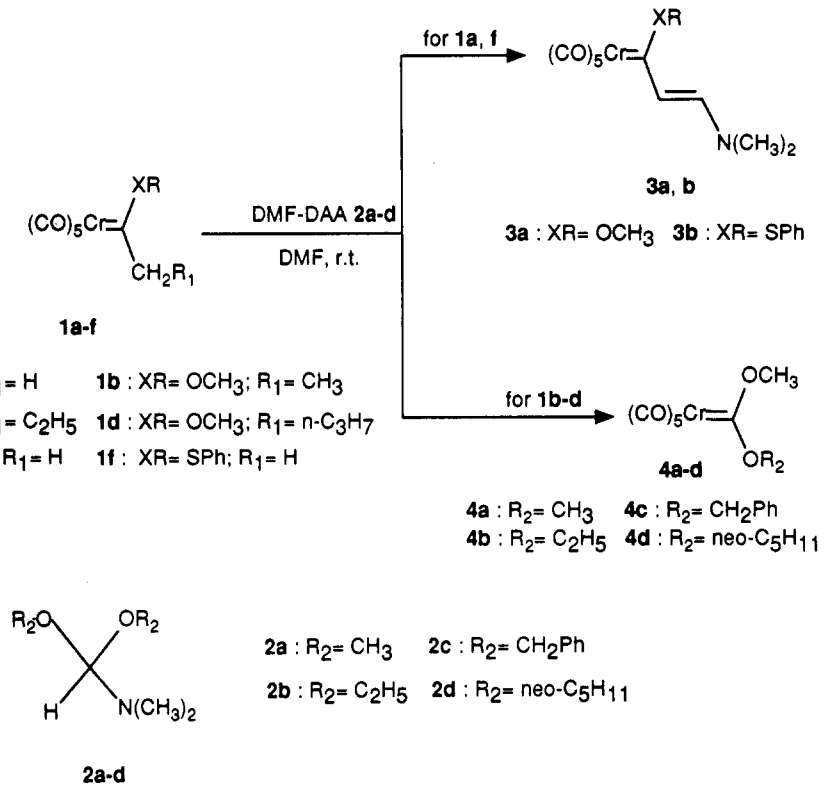
Scheme I



reaching 14% in the case of compound **7d** (see Table I). By carefully repeating the reaction of **5b** with DMF–DMA, we were able to isolate the new pentacarbonylchromium carbene complex **7b** (yield 4%) as well as **6b**, but with compounds **5e** and **5f** no traces of the cyclopropyl derivatives were detected, and only the expected enamine derivatives **6e,f** were isolated. The structure of compounds **7a–d** was based on spectroscopic and analytical data (see Tables I–III). The *E* stereochemistry of the newly formed carbon–carbon double bond was confirmed by the X-ray analysis of a single crystal of product **8**,[9] independently synthesized through the reaction of complex **5b** with cyclopropanecarbaldehyde in the presence of triethylamine (Scheme II, bottom).[10] Under the same reaction conditions, **5a** led to the corresponding **7a**.

Although the yields of compounds **7a–d** are low, the mechanism of their unexpected formation is interesting. It is noteworthy that the same substitution pattern of the five membered ring in complexes **5a–d** is found on the cyclopropyl unit in complexes **7a–d**; this, together with the recovery of $Cr(CO)_6$ from the reaction mixture, is consistent with the hypothesis that the cyclopropyl residue arises from a ring contraction of the five membered ring of complexes **5**. In order to explain the formation of a cyclopropane derivative during the course of the reaction, we propose the mechanism reported in Scheme III. In DMF solution, DMF–DMA is partially dissociated into the methoxide ion and the *N,N*-dimethylimmonium ion **9**; the methoxide ion deprotonates complexes **5** and the resulting conjugate bases then react with **9**, giving the nonisolable intermediates **10**. These intermediates can eliminate a molecule of methanol to give carbenes **6** (path a, Scheme III). Alternatively, the nucleophilic attack of a methoxy group on the electrophilic carbene carbon atom of **10** may encourage the breaking of the bond between the carbene carbon and the α-carbon atoms, leading to the formation of enamine derivatives **11** (path b, Scheme III). Intramolecular β-alkylation[11] then provides the metal acyl anion **12** which evolves into $Cr(CO)_6$ as a result of the elimination of the methoxide ion. The dimethylimmonium ion **13** is formed on the other side. This reacts with the starting carbenes **5** and provides the cyclopropylmethylidene derivatives **7**.[13] Support for the formation of compounds **7** from **5** and **13** comes from the reaction we created between carbene **5b** and the "in situ" generated aminal of cyclopropanecarbaldehyde by mixing an equimolar amount of aldehyde, dimethylamine hydrochloride, triethylamine, and potassium carbonate in DMF solution at room temperature, with the later addition of carbene **5b**. The reaction is very fast, and a 70% yield of compound **8** was recovered.[14]

Further support for the mechanism shown in Scheme III is given by the reaction between the 4,4-dimethyl substituted carbene **5g**[15] and DMF–DMA (Scheme IV). Although this reaction apparently does not give any of the expected products (i.e., the enamine carbene and/or the cyclopropyl derivative), treatment of the reaction solution with (2,4-dinitrophenyl)hydrazine does give rise to the formation of the (2,4-dinitrophenyl)hydrazone of 2,2-

(9) We thank Dr. David Williams (Imperial College, London) for his personal communication.
(10) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.
(11) Intermolecular β-alkylation of enamines is a well-known reaction.[12]
(12) Cook, G. A. *Enamines: Synthesis, structure, and reactions*; Marcel Dekker Ltd.: New York, 1969; p 119.
(13) Compounds **7c** and **7d** have been isolated as single diastereoisomers and, apparently, no traces of other stereoisomers have been detected. However, due to the very low yields of compounds **7**, we would not make any comment about this stereochemical result.
(14) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437.
(15) This compound has been prepared following a new procedure we set up recently.[16]
(16) Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti-Gerosa, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1623.

Scheme II

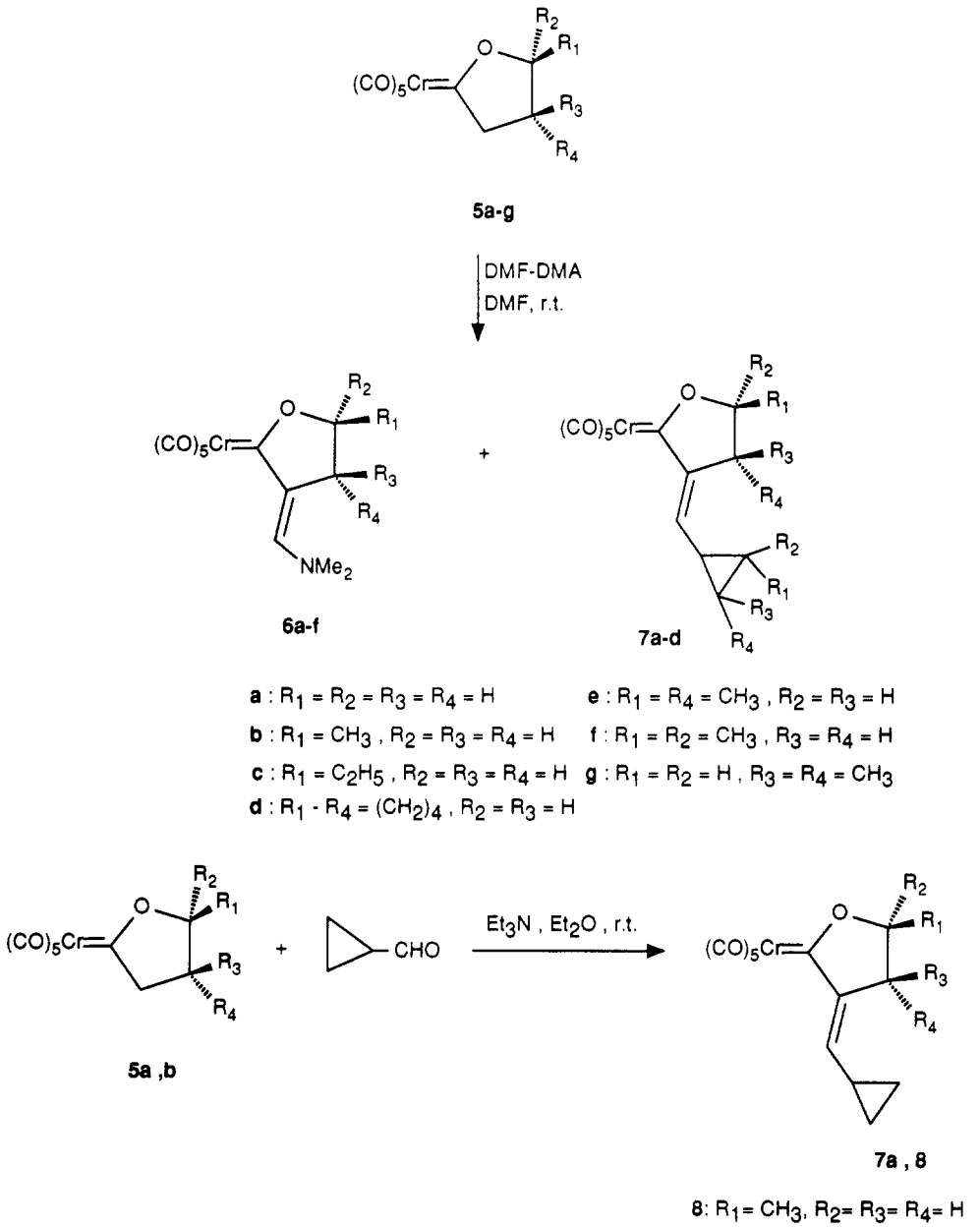


Table I. Reaction Yields and Physical Data for Compounds 6a–f and 7a–d

compd	yield (%)	mp t/°C	mol formula	m/e	anal. found (calcd) C	H	N
6a	66.5	113[a]	$C_{12}H_{11}CrNO_6$	317	45.78 (45.43)	3.73 (3.47)	4.85 (4.42)
6b	71	114[a]	$C_{13}H_{13}CrNO_6$	331	47.57 (47.13)	4.07 (3.95)	4.12 (4.22)
6c	64	114[a]	$C_{14}H_{15}CrNO_6$	345	48.57 (48.70)	4.47 (4.38)	4.14 (4.05)
6d	5	105[a]	$C_{16}H_{17}CrNO_6$	371	51.95 (51.75)	4.85 (4.58)	3.65 (3.77)
6e	42	93[a]	$C_{14}H_{15}CrNO_6$	345	48.83 (48.70)	4.37 (4.38)	3.88 (4.05)
6f	41	129[a]	$C_{14}H_{15}CrNO_6$	345	48.28 (48.70)	4.29 (4.38)	4.13 (4.05)
7a	2	91[a]	$C_{13}H_{10}CrO_6$	314	50.06 (49.68)	3.34 (3.18)	
7b	4	67[b]	$C_{15}H_{14}CrO_6$	342	52.91 (52.63)	4.25 (4.09)	
7c	1.5	oil	$C_{17}H_{18}CrO_6$	370	55.52 (55.13)	5.13 (4.86)	
7d	14	150[c]	$C_{21}H_{22}CrO_6$	422	58.19 (59.71)	5.58 (5.21)	

[a] Crystallized from diethyl ether/*n*-pentane at −78 °C. [b] Crystallized from *n*-pentane at −78 °C. [c] Crystallized from *n*-pentane.

dimethylcyclopropanecarbaldehyde (**14**).[17] This experimental result clearly shows the reasonableness of the hypothesis of the formation of a reactive derivative such as **13** in Scheme III. We believe that, in the case of complex **5g**, a derivative of the 2,2-dimethylcyclopropanecarbaldehyde analogous to **13** does not react because of steric hindrance due to the presence of two methyl groups (on **5g** and on the aldehyde itself).

It is worth noting that the unexpected behavior of carbene complexes **5a–d** in the reaction with DMF–DMA is very similar to the behavior we observed in the reaction of pentacarbonyl(alkoxyalkylcarbene)chromium complex-

(17) Julia, M.; Julia, S.; Duchaffaut, J. A. *Bull. Soc. Chim. Fr.* **1960**, 1735.

Table II. ^{1}H NMR Data for Compounds 6a,c-f and 7a-d

compd	^{1}H NMR δ, ppm
6a	2.9 (t, 2H, J_{vic} = 9 Hz, Cr=CCCH_2CH$_2$O–), 3.3 [s, 6H, –N(CH$_3$)$_2$], 4.65 (t, 2H, J_{vic} = 9 Hz, Cr=CCCH$_2$CH_2O–), 7.9 [s, 1H, =CH—N(CH$_3$)$_2$]
6c	1.00 (t, 3H, J_{vic} = 6 Hz, –OCHCH$_2$CH_3), 1.65 (quintet, 2H, J'_{vic} = J''_{vic} = 6 Hz, –OCHCH_2CH$_3$), 2.45 [dd, 1H, J_{gem} = 13.5 Hz, J_{vic} = 6 Hz, Cr=CCC(H)HCHO–], 2.95 [dd, 1H, J_{gem} = 13.5 Hz, J_{vic} = 9 Hz, Cr=CCCH(H)CHO–], 3.30 [s, 6H, –N(CH$_3$)$_2$], 4.80 (m, 1H, Cr=CCH$_2$CHO–), 7.80 [s, 1H, =CH—N(CH$_3$)$_2$]
6d	1.20–2.5 (m, 9H, Cr=CCCHCHO– + cyclohexyl), 3.25 [s, 6H, –N(CH$_3$)$_2$], 3.75 (m, 1H, Cr=CCCHCHO–), 7.97 [s, 1H, =CH—N(CH$_3$)$_2$]
6e	1.05 [d, 3H, J_{vic} = 7.5 Hz, Cr=CCCH(CH_3)CHO–], 1.25 [d, 3H, J_{vic} = 7.5 Hz, Cr=CCCHCH(CH_3)O–], 2.65 (m, 1H, Cr=CCCHCHO–), 3.3 [s, 6H, –N(CH$_3$)$_2$], 4.6 (dq, 1H, J'_{vic} = 2.5 Hz, J''_{vic} = 7.5 Hz, Cr=CCCHCHO–), 7.9 [s, 1H, =CH—N(CH$_3$)$_2$]
6f	1.45 [s, 6H, Cr=CCCH$_2$C(CH_3)$_2$O–], 2.70 (s, 2H, Cr=CCCH$_2$CO–), 3.25 [s, 6H, –N(CH$_3$)$_2$], 7.8 [s, 1H, =CH—N(CH$_3$)$_2$]
7a	0.98 (dt, 2H, J_{gem} = J'_{vic} = 12 Hz, J''_{vic} = 4.5 Hz, –CH$_2$–, cyclopropyl), 1.28 (dt, 2H, J_{gem} = J'_{vic} = 12 Hz, J''_{vic} = 3 Hz, –CH$_2$–, cyclopropyl), 1.64 (m, 1H, Cr=CC=CHCH–, cyclopropyl), 2.79 (dt, 2H, J_{vic} = 9 Hz, $J_{allylic}$ = 3 Hz, Cr=CCCH_2CH$_2$O–), 4.91 (t, 2H, J_{vic} = 9 Hz, Cr=CCCH$_2$CH_2O–), 6.75 (dt, J_{vic} = 11.3 Hz, $J_{allylic}$ = 3 Hz, Cr=CC=CH—cyclopropyl)
7b	1.2 (d, 3H, J_{vic} = 5 Hz, –CHCH_3, cyclopropyl), 1.5 [d, 3H, J_{vic} = 6 Hz, Cr=CCCH$_2$CH(CH_3)O–], 0.9–1.7 (m, 4H, cyclopropyl), 2.3 [m, 1H, Cr=CCC(H)HCHO–], 2.9 [m, 1H, Cr=CCCH(H)CHO–], 5.15 (m, 1H, Cr=CCCH$_2$CHO–), 6.7 (d, 1H, $J_{allylic}$ = 2.4 Hz, J_{vic} = 10 Hz, Cr=CC=CH—cyclopropyl)
7c	1.0–1.90 (m, 14H, –CH$_2$CH_3, –CH_2CH$_3$, cyclopropyl), 2.33 [ddd, 1H, J_{gem} = 15.8 Hz, J_{vic} = 6 Hz, $J_{allylic}$ = 2.4 Hz, Cr=CCC(H)HCHO–], 2.80 [ddd, 1H, J_{gem} = 15.8 Hz, J_{vic} = 8.8 Hz, $J_{allylic}$ = 2.4 Hz, Cr=CCCH(H)CHO–], 5.05 (m, 1H, OCHCH$_3$), 6.7 (dt, 1H, J_{vic} = 10.3 Hz, $J_{allylic}$ = 2.4 Hz, Cr=CC=CH—cyclopropyl)
7d	1.1–2.5 (m, 20H, cyclohexyl, cyclopropyl, Cr=CCCHCHO–), 3.92 (dt, 1H, J_{cis} = 3.9 Hz, J_{trans} = J'_{trans} = 12.2 Hz, Cr=CCCHCHO–), 6.57 (dd, 1H, J_{vic} = 11.5 Hz, $J_{allylic}$ = 3 Hz, Cr=CC=CH—cyclopropyl)

Table III. IR Spectral Data for Complexes 6a–f and 7a–d

complex	ν, cm^{-1} (Nujol)
6a	2050, 1975, 1945 (broad), 1620
6c	2060, 1980, 1950 (broad), 1630
6d	2050, 1975, 1940 (broad), 1620
6e	2050, 1980, 1940 (broad), 1620
6f	2050, 1980, 1950 (broad), 1639
7a	2050, 1980, 1950 (broad), 1630
7b	2040, 1975, 1945 (broad), 1625
7c	2055, 1980, 1950 (broad), 1630
7d	2070, 2000, 1955 (broad), 1635

es **1b–d** with DMF–DAA **2a–d**, where the formation of pentacarbonyl(dialkoxycarbene)chromium derivatives **4a–d** occurred in fair to good yields (Scheme I).[6] Also in this case, we propose a mechanism in which the formation of an enamine is involved.

As shown in Scheme V, complexes **1a–d** react with DMF–DAA **2a–d** to give the intermediate adducts **15** which, in the case of carbene **1a** (R$_1$ = H), evolve to the enamine derivative **3a** through the elimination of a molecule of alcohol R$_2$OH (path a, Scheme V). As already reported,[6] X-ray analysis of a single crystal of compound **3a** shows the *E* configuration of the carbon–carbon double bond. We cannot exclude the formation of the *Z* isomer; however, possible isomerization into the thermodynamically more stable *E* isomer could take place through the addition–elimination of methanol to the double bond during the course of the reaction.[10]

On the contrary, all of the carbenes **1b–d** produce a different reaction product, namely the pentacarbonyl(dialkoxycarbene)chromium complexes (**4a–d**). To explain the formation of these compounds, we can once again hypothesize the nucleophilic attack of an alkoxy group on the electrophilic carbene carbon atom of **15**, with cleavage of the bond between the carbene carbon atom and the α-carbon and the formation of nonisolated enamine derivatives **16** (path b, Scheme V). However when R$_1$ = *n*-C$_3$H$_7$ (complex **1d**), it was possible to trap the corresponding enamine as a mixture of the cycloadducts **17** and **18**, by running the reaction of **1d** with the *N,N*-dimethylformamide dineopentyl acetal **2d** in the presence of *p*-nitrophenyl azide (Scheme V). Compound **17** was then oxidized to triazoline **18** by means of the exposure of an ethereal solution of **17** to air and sunlight (see Experimental Section). Compound **18**, not previously reported in the literature, was finally identified by means of a comparison with an authentic sample idependently synthesized following a procedure reported for analogous compounds (see Experimental Section).[18]

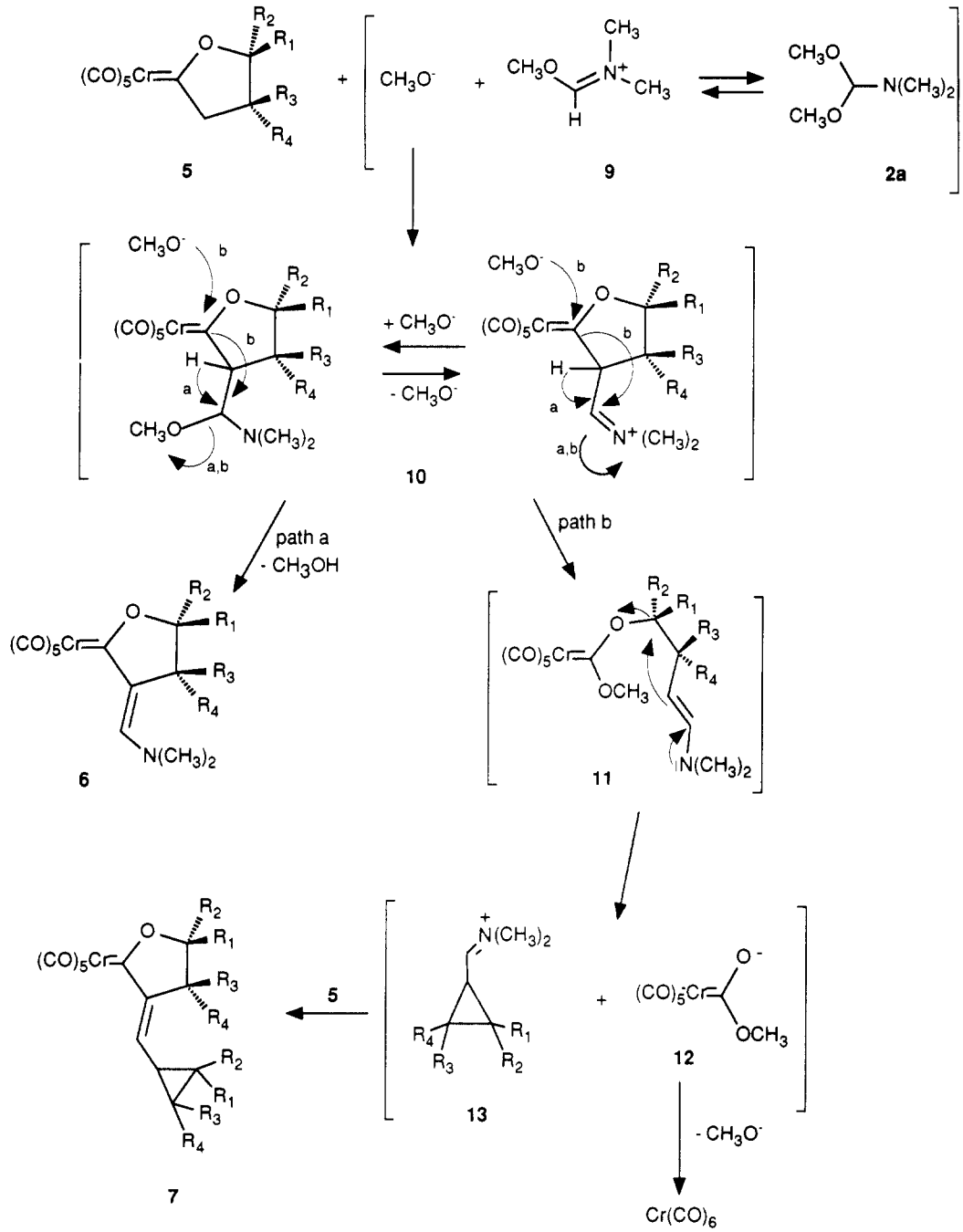
The difference in behavior between carbenes **1b–d** and **1a** may be attributable to a steric hindrance due to the presence of the alkyl chain on the α-carbon atom preventing access to the hydrogen atom of the same carbon and enabling the formation of dialkoxycarbene complexes **4a–d** from intermediates **15**.

The fact that it has been possible to explain and show the formation of both compounds **4** and the enamine **16** in the above reactions in a satisfactory manner strongly supports the formation of the enamine intermediate **11** from carbenes **5** (Scheme III). In this case, **11** is probably not trapped because the intramolecular β-alkylation that forms the cyclopropane ring is the favored process.

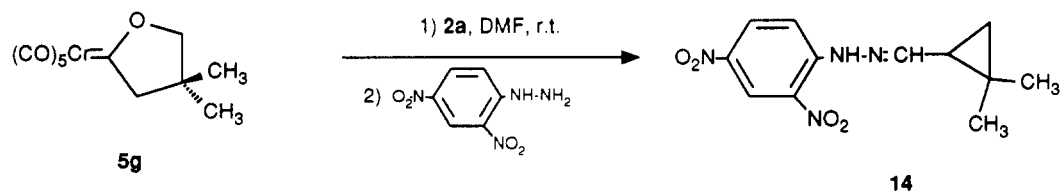
The reaction with DMF–DMA was extended to carbenes **1e** and **1f**, in which a different heteroatom is present, respectively nitrogen and sulfur (Scheme I). The aminocarbene complex **1e** did not react at all with **2a** even after heating at 100 °C in DMF solution for several hours. Probably, the methoxide ion is not a sufficient base to deprotonate the less acidic aminocarbene **1e** and, therefore, the corresponding conjugate base cannot be formed under these reaction conditions. On the contrary, **1f** reacted

(18) Stradi, S.; Pocar, D.; Bianchetti, G. *Org. Magn. Reson.* **1972**, *4*, 248.

Scheme III



Scheme IV



with DMF–DMA very quickly in mild conditions to give the complex **3b**.

Finally, we would like to draw particular attention to the high-field resonance in the ^{13}C NMR spectra for the carbene carbon atom of enamine carbene complexes **3a**, **3b**, **6a**, and **6b** (Table IV). This reflects the lower electrophilic character of the carbene carbon atom as a consequence of the additional stabilization of the molecule due to the π-donor ability of the nitrogen atom, which increases the number of resonance structures.

Conclusion

Fischer type carbene complexes **1** and **5** react smoothly with the *N,N*-dimethylformamide dialkyl acetals, the nature of the reaction products depending on the structure of the starting complexes. In the case of pentacarbonyl-

Scheme V

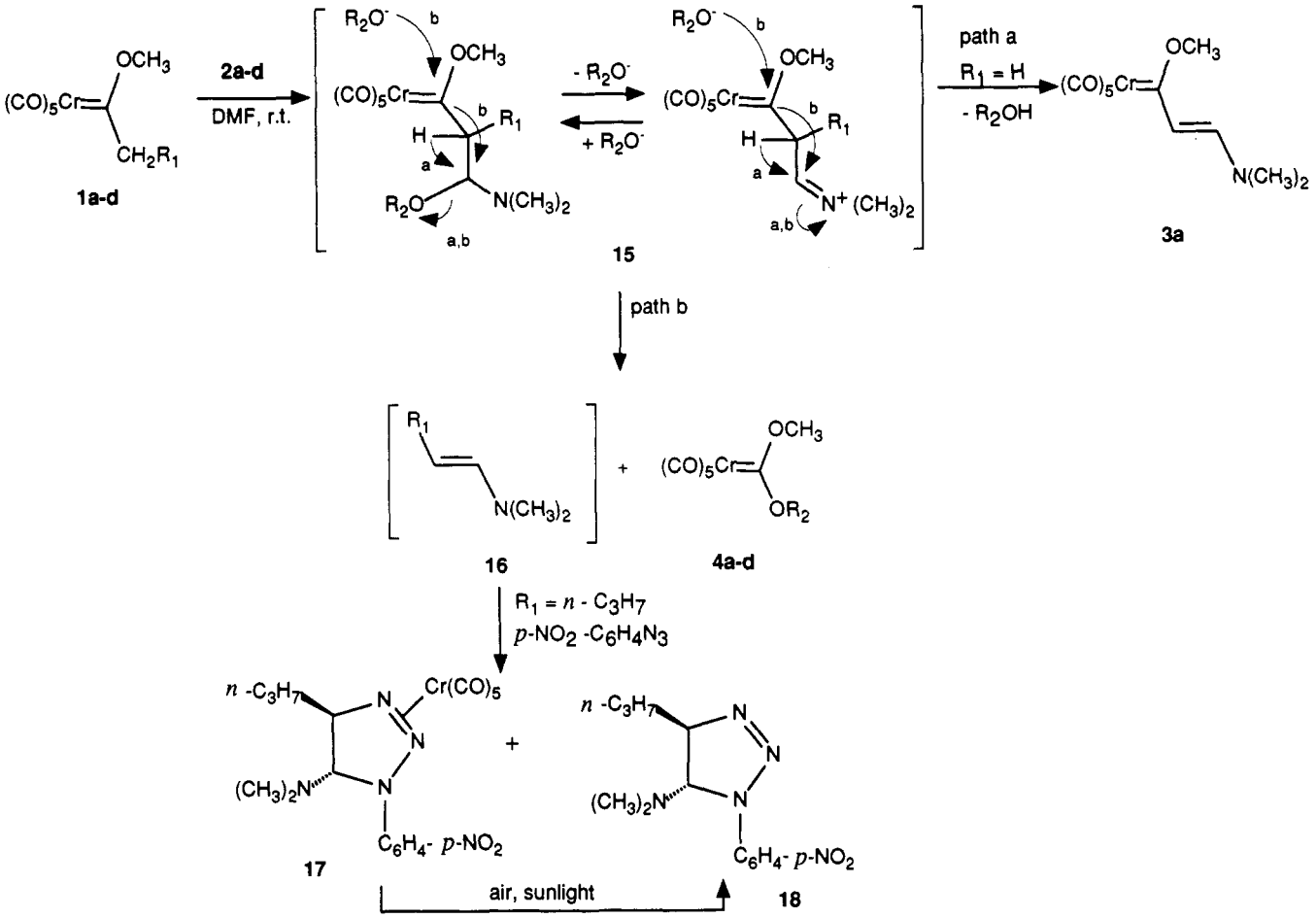


Table IV. ^{13}C NMR Data for Complexes 1a, 1f, 3a, 3b, 5a, 5b, 6a, 6b

complex	$C_{carbene}$	C_{M-CO} trans	C_{M-CO} cis	all other C atoms
1a	362.3	223.6	217.6	67.2, 49.1
1f	367.3	227.5	216.2	136.5, 131.8, 130.6, 130.0, 47.3
3a	288.5	224.0	219.5	169.5, 109.5, 58.5, 45.5
3b	272.4	224.7	219.1	163.8, 135.5, 129.5, 129.4, 120.4, 46.8, 37.9
5a	342.7	223.3	216.4	85.4, 60.7, 27.8
5b	340.2	223.4	216.4	95.9, 60.9, 28.1, 20.5
6a	284.8	223.8	219.1	162.2, 125.5, 78.2, 47.8
6b	283.8	223.8	219.2	162.2, 125.2, 86.9, 47.0, 38.0, 33.6, 22.1

(alkoxyalkylcarbenes)chromium **1a–d**, the reaction with **2a–d** can take two different routes, depending on the nature of the R_1 group; when R_1 = H, the expected complex **3a** is obtained, but when R_1 = alkyl, a striking result is obtained: the formation of dialkoxy complexes **4**. This latter reaction represents a new and general method for the synthesis of complexes **4**,[19] which can be regarded as analogs of dialkyl carbonates; studies of their reactivity are now under investigation in our laboratory.

On the other hand, from the cyclic carbene complexes **5a–d** a mixture of enamine complexes **6a–d** and cyclopropyl complexes **7a–d** are obtained.

We have shown that both complexes **4** and **7** originate from the attack of an alkoxy group on the electrophilic carbene carbon of intermediates **15** (Scheme V) and **11** (Scheme III), formed from the reaction of the α-anions of the carbene complexes **1** and **5** with DMF–DAA. The nucleophilic attack promotes the fission of the bond between the carbene carbon and the α-carbon atom. To the best of our knowledge, this behavior is unprecedented in the chemistry of Fischer type carbene complexes.

Experimental Section

General Comments. All melting points were obtained with a Büchi apparatus and are uncorrected. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian EM 390 (90 MHz), XL 200 (200 MHz); ^{13}C NMR, Varian XL 200, 300 (200, 300 MHz). Chemical shifts are reported in δ (Me_4Si as internal standard with a Varian EM 390 instrument, $CDCl_3$ in all other cases). IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Mass spectra were taken with a Varian MAT 311-A spectrophotometer equipped with a combined EI-FI-FD ion source. All chromatographic purifications were accomplished by flash column chromatography with silica gel 60 (230–400 mesh). All samples were filtered on Millex-SR 0.5-μm filters (Millipore Waters) before NMR measurements.

Materials. Dimethylformamide used for reactions was dried by filtration on an Al_2O_3 pad just before use. Pentacarbonyl-(2-oxacyclopentylidene)chromium compounds **5a–f** were synthesized according to our previous reported procedure.[5] Pentacarbonyl(4,4-dimethyl-2-oxacyclopentylidene)chromium (**5g**) was synthesized through a new procedure we published recently.[16]

(19) Only two papers have reported the synthesis of complex **4a**,[20] obtained however through completely different methods.

(20) Fischer, E. O.; Scherzer, K.; Kreissl, F. R. *J. Organomet. Chem.* **1976**, *118*, C33. Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.

Complexes **1a–f** are known compounds: **1a**,[21] **1b**,[22] **1c**,[23] **1d**,[24] **1e**,[25] **1f**.[21] The synthesis of compounds **4a–c** has already been reported.[6]

General Procedure for the Reaction between Complexes 5a–f and DMF–DMA (2a): Synthesis of Pentacarbonyl(2-oxacyclopentylidene)chromium(0) 6a–f and 7a–d. To a solution of **5a–f** (3 mmol) in anhydrous DMF (10 mL) was added the *N,N*-dimethylformamide dimethyl acetal (3 mmol). The reaction was allowed to proceed at 20 °C under argon, until the complete disappearance of **5a–f** (TLC analyses on silica gel; eluent, petroleum ether/diethyl ether 1:1). The mixture was then diluted with water (100 mL) and extracted with diethyl ether (3 × 100 mL). The ethereal layer was dried (Na_2SO_4) and evaporated under reduced pressure. The products were separated by flash column chromatography on silica gel (eluent, petroleum ether/diethyl ether 4:1) and purified by crystallization, as indicated in Table I.

Condensation of Cyclopropanecarbaldehyde with Complexes 5a,b: Synthesis of Compounds 7a and 8. To a solution of complexes **5a,b** (1 mmol), in diethyl ether (20 mL), was added at room temperature a solution of cyclopropanecarbaldehyde (1 mmol) and triethylamine (0,4 mL) in 10 mL of diethyl ether. The mixture was allowed to react at the same temperature for 24 h. The solvent was distilled off, and the crude reaction mixture was taken up with diethyl ether. The insoluble residue was filtered off and the solvent removed under reduced pressure. **7a** (0.223 g, 90%) and 0.24 g of **8** (70%) were recovered by crystallization of the residue from *n*-pentane at −78 °C.

Data for **7a**: red crystals, mp 88–89 °C; IR (Nujol) (cm^{-1}) 2030 ν(CO), 2000 ν(CO), 1960–1870 (broad) ν(CO), 1635 ν(C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 0.98 (dt, 2H, J_{vic} = 4.5 Hz, J_{gem} = 12 Hz, CH_2, cyclopropyl), 1.28 (dt, J_{vic} = 3 Hz, J_{gem} = 12 Hz, CH_2, cyclopropyl), 1.64 (m, 1H, CH, cyclopropyl), 2.79 (dt, 2H, $J_{allylic}$ = 3 Hz, J_{vic} = 9 Hz, Cr=CCCH_2CH_2O–), 4.91 (t, 2H, J_{vic} = 9 Hz, Cr=C-CCH_2CH_2O–), 6.75 (dt, 1H, $J_{allylic}$ = 3 Hz, J_{vic} = 11.3 Hz, Cr=CC=CH—cyclopropyl).

Data for **8**: red crystals, mp 71–73 °C; IR (Nujol) (cm^{-1}) 2060 ν(CO), 1980–1889 (broad) ν(CO), 1625 ν(C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 0.8–1.0 (m, 2H, CH_2 cyclopropyl), 1.1–1.3 (m, 2H, CH_2, cyclopropyl), 1.4–1.65 (m, 1H, CH, cyclopropyl), 1.5 [d, 3H, J_{vic} = 6 Hz, Cr=CCCH_2CH(CH_3)O–], 2.25 [ddd, 1H, $J_{allylic}$ = 2.5 Hz, J_{vic} = 6 Hz, J_{gem} = 15 Hz, Cr=CCCH(*H*)CHO–], 2.90 [ddd, 1H, $J_{allylic}$ = 2.5 Hz, J_{vic} = 9 Hz, J_{gem} = 15 Hz, Cr=CCC(*H*)-HCHO–], 5.15 (m, 1H, Cr=CCH_2C*H*—O), 6.65 (dt, 1H, $J_{allylic}$ = 2.5 Hz, J_{vic} = 10 Hz, Cr=CC=CH—cyclopropyl); MS *m/e* 328 (M^+). Anal. Calcd for $C_{14}H_{12}CrO_6$: C, 51.22; H, 3.93. Found: C, 50.90; H, 3.68.

Reaction of 5g with DMF-DMA (2a): Isolation of the (2,4-Dinitrophenyl)hydrazone of 2,2-Dimethylcyclopropanecarbaldehyde 14. To a dimethylformamide solution (3 mL) of **5g** (1 mmol) was added at room temperature DMF-DMA (1 mmol). The mixture was allowed to react at the same temperature for 72 h (during this time $Cr(CO)_6$ separated from the reaction mixture). The $Cr(CO)_6$ formed was filtered off and the solution treated with a 1% aqueous solution of (2,4-dinitrophenyl)-hydrazine and extracted two times with 50 mL of dichloromethane. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography yielding 17 mg (6%) of **14** as an orange solid, crystallized from $CHCl_3$/MeOH: mp 163–165 °C (lit.[17] 166–168 °C); IR (Nujol), (cm^{-1}) 3285 ν(NH), 1623 ν(C=N); ^1H NMR (80 MHz, $CDCl_3$) δ 1.0 (m, 2H, cyclopropyl), 1.26 (s, 6H, $2CH_3$), 1.64 (m, 1H, CH, cyclopropyl), 7.25 (d, 1H, J_{vic} = 7.7 Hz, –N=C*H*–), 7.90 (d, 1H, arom, J_{ortho} = 10.3 Hz), 8.26 (dd, 1H, arom, J_{meta} = 2.6 Hz, J_{ortho} = 10.3 Hz), 9.09 (d, 1H, arom, J_{meta} = 2.6 Hz), 11.0 (bs, 1H, NH); MS *m/e* 278 (M^+). Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.04; N, 20.14. Found: C, 51.65; H, 5.11; N, 19.28.

Reaction of 1d with Dimethylformamide Dineopentyl Acetal (2d): Synthesis of 4d and Isolation of the (*p*-Nitrophenyl)-4-*n*-propyl-5-(dimethylamino)-Δ²-1,2,3-triazoline 18. To a solution of **1d** (3.5 mmol) in anhydrous DMF (10 mL) was added *N,N*-dimethylformamide dineopentyl acetal (36 mmol). After 4 h at room temperature *p*-nitrophenyl azide (3.5 mmol) was added. The mixture was allowed to react a further 1 h and was then diluted with water and extracted with diethyl ether (2 × 100 mL). The ethereal layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash chromatography (eluents, petroleum ether/CH_2Cl_2 8:2, petroleum ether/CH_2Cl_2 1:1, and CH_2Cl_2).

Three fractions were recovered: 0.61 g of complex **4d** (56%), 0.132 g of complex **17** (8%), and 0.427 g of compound **18** (46%). Data for **18**: mp 105 °C (ethanol); IR (Nujol) (cm^{-1}) 1590 ν(N=N); ^1H NMR (90 MHz, $CDCl_3$) δ 0.9–1.8 (m, 7H, *n*-propyl), 2.15 [s, 6H, –N(CH_3)$_2$], 4.4–4.6 (m, 2H, CH—CH), 7.41 (d, 2H, arom, J_{ortho} = 9 Hz), 8.15 (d, 2H, arom, J_{ortho} = 9 Hz); ^{13}C NMR (300 MHz) δ 145.92 (=C—NN=N), 142.71 (–C—NO_2), 125.63 (–*C*—C—NO_2), 114.85 (–*C*—C—C—NO_2), 78.05 [(CH_3)$_2$N—*C*H], 74.95 [(CH_3)$_2$N—CH—*C*H], 37.76 [(CH_3)$_2$N–], 34.58 (–*C*H$_2$—CH_2—CH_3), 18.89 (–CH_2—*C*H$_2$—CH_3), 13.89 (–CH_2—CH_2—*C*H$_3$). Anal. Calcd for $C_{13}H_{19}N_5O_2$: C, 56.30; H, 6.90; N, 25.25. Found: C, 56.71; H, 7.21; N, 25.15.

Compound **17**, dissolved in 10 mL of diethyl ether, was oxidized with air in the presence of sunlight for 5 h. The solution was filtered over a pad of Celite and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent, diethyl ether/petroleum ether 1:1), yielding 19 mg of **18** (25%).

Synthesis of 1-(*p*-Nitrophenyl)-4-*n*-propyl-5-(dimethylamino)-Δ²-1,2,3-triazoline (18). To a solution of 1-(*N,N*-dimethylamino)-1-pentene in chloroform (20 mL) [prepared in situ from pentanal (18 mmol), dimethylamine hydrochloride (39.3 mmol), and triethylamine (39.8 mmol)] was added *p*-nitrophenyl azide (9.4 mmol). The mixture was stirred at room temperature for 24 h and filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (eluent, diethyl ether/petroleum ether 1:1), yield 0.52 g of **18** (20%). Mp: 105 °C (ethanol).

IR (Nujol) (cm^{-1}): 1590 ν(N=N). ^1H NMR (90 MHz, $CDCl_3$): δ 0.9–1.8 (m, 7H, *n*-propyl), 2.15 [s, 6H, –N(CH_3)$_2$], 4.4–4.6 (m, 2H, –CH—CH–), 7.41 (d, 2H, arom, J_{ortho} = 9 Hz), 8.15 (d, 2H, arom, J_{ortho} = 9 Hz). Anal. Calcd for $C_{13}H_{19}N_5O_2$: C, 56.30; H, 6.90; N, 25.25. Found: C, 56.43; H, 7.01; N, 25.35.

Reaction of 1f with DMF-DMA. The reaction was performed by following the procedure already reported by us.[6] To a solution of **1f** (1 mmol) in anhydrous DMF (15 mL) was added *N,N*-dimethylformamide dimethyl acetal (1 mmol) at room temperature. The reaction was allowed to react at the same temperature until disappearance of the starting carbene (TLC analyses on silica gel; eluent, diethyl ether/petroleum ether 1:1). The reaction mixture was diluted with water (50 mL), extracted four times with 50 mL of diethyl ether, and dried over Na_2SO_4. The solvent was distilled off under reduced pressure and the residue purified by flash chromatography (eluent, diethyl ether/petroleum ether 1:1), yielding 0.17 g of **3b** (26%) as the *E* isomer.

Data for **3b**: orange crystals, dec 120 °C; IR (Nujol) (cm^{-1}) 2050 ν(CO), 1980–1900 (broad) ν(CO), 1610 ν(C=C); ^1H NMR (80 MHz, $CDCl_3$) δ 2.75 (s, 3H, NCH_3), 3.33 (s, 3H, NCH_3), 6.33 [d, 1H, J_{trans} = 12 Hz, Cr=CC*H*=CH—N(CH_3)$_2$], 7.35 (m, 5H, Ph), 7.93 [d, 1H, J_{trans} = 12 Hz, Cr=CCH=C*H*—N(CH_3)$_2$]; MS *m/e* 383 (M^+). Anal. Calcd for $C_{16}H_{13}CrNO_5S$: C, 50.08; H, 3.39; N, 3.65. Found: C, 51.62; H, 3.66; N, 3.11.

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