Photochemistry of Imine−Group VI Carbene Complexes: Novel Reactivity Involving a Cyclopentannulation Reaction†

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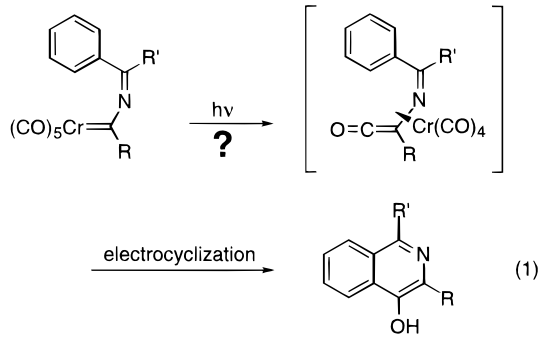
3-Aza-1-chroma-1,3-butadiene undergoes photochemical [3 + 2] cyclopentannulation with alkenes and alkynes instead of the expected benzannulation or cyclobutannulation reactions, providing a good method for the synthesis of 1-pyrroline and 2*H*-pyrrole derivatives. This photochemical reaction can be extended to molybdenum and tungsten carbene complexes.

Introduction

In recent years, much attention has been paid to studies of the photochemical addition reactions of group VI carbene complexes.[1,2] The general accepted mechanism for the photochemical reactions of Fischer carbene complexes involves in the first step CO insertion into the Cr=C bond to form a coordinated ketene followed by reaction with the substrate.[1,2] Some of the photoreactions reported use metalladienes and metallatrienes as the starting complex, but as far as we know, despite the fact that some useful thermally driven reactions of imino carbene complexes of tungsten and chromium have been reported,[3] only one photochemical reaction of 3-aza-1-metalla-1,3-dienes has been described.[4] In this case, the reaction of *O*-acylimidato carbene complexes with imines occurs with formation of several different four-membered cyclic products and its utility is very limited. Since we have some experience in procedures involving light-induced electrocyclization reactions of unsaturated imines,[5,6] we found it of interest to study the photochemical behavior of Fischer carbene complexes having an imine group on the carbene carbon. As shown in eq 1, the irradiation of

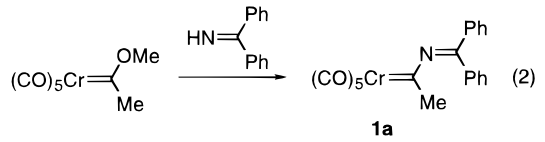


(1)

appropriate imine−carbene complexes could lead to an electrocyclic ring closure. Herein, we wish to report our preliminary results on the light-induced reactivity of these complexes.

Results and Discussion

First, we prepared the imine carbene complex **1a** by direct reaction of (methoxymethylcarbene)pentacarbonylchromium(0) with benzophenone imine in Et_2O at room temperature under an inert atmosphere (eq 2).[7]



(2)

1a

After purification by column chromatography, we carried out the direct irradiation of **1a** with a medium-pressure mercury lamp using THF as solvent until the complete consumption of starting carbene (2 h for 0.25 mmol of **1a**, monitored by ^{1}H NMR spectroscopy). Chromatographic workup of the resulting crude product afforded a 25% yield of the 2-aza-1,3-butadiene derivative **2a** (Scheme 1) together with a large amount of polymeric material, instead of the electrocyclization product expected (see eq 1). To explain the formation of **2a**, we can postulate a metathesis reaction between the carbene Cr=C bond and the imine N=C bond of the other molecule (Scheme 1). After imine coordination (**A**),

† Dedicated to Prof. José Barluenga on the occasion of his 60th birthday.

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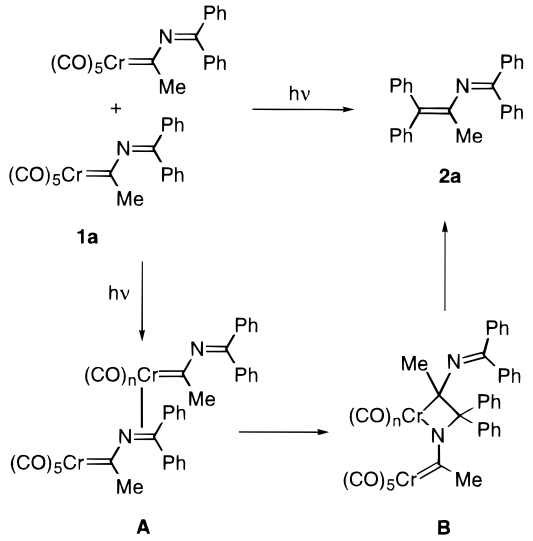
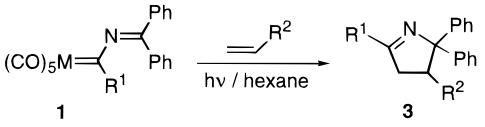
Scheme 1



Scheme 2



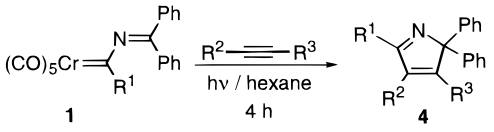
	M	R^1	R^2	t (h)		Yield (%)
1a	Cr	Me	CO_2Et	2	**3a**	54
1a	Cr	Me	COMe	2	**3b**	76
1a	Cr	Me	Ph	2	**3c**	21
1b	Cr	Ph	COMe	2	**3d**	61
1c	Mo	Me	COMe	5	**3b**	54
1d	W	Me	CO_2Et	5	**3a**	43
1d	W	Me	COMe	5	**3b**	50

the [2 + 2] addition should give an azametallacycle (**B**), which evolves with formation of **2a**. The regiospecificity obtained is consistent with prior observations in related systems.[8]

The postulated [2 + 2] addition prompted us to study the photoreaction of **1a** in the presence of an alkene. We therefore carried out the irradiation of **1a** and ethyl acrylate with a medium-pressure mercury lamp. Chromatographic workup of the resulting crude product afforded the 1-pyrroline derivative **3a** (Scheme 2), as identified by its spectroscopic data (^{1}H and ^{13}C NMR) and mass spectrometry. The reaction gave a single regioisomer, and the configuration assignment was made on the basis of difference NOESY experiments (positive NOE of H_{OEt} with H_{Ph}; see Scheme 2). A range of solvents (THF, Et_2O) can be used in the photoreaction, although the best results were obtained by irradiation in hexane through Pyrex glass and 10 equiv of alkene.

Encouraged by this result, we decided to expand the applicability of this process by using other carbene complexes and unsaturated systems to study its scope and synthetic possibilities. As is also indicated in Scheme 2, the reaction could be extended to different substituted carbene complexes and alkenes to give moderate to good yields of 1-pyrroline derivatives **3**. The configuration assignment shown in Scheme 2 was made on the basis of difference NOESY experiments (**3b**, positive NOE of H_{COMe} with H_{Ph}) or by comparison with the ^{1}H and ^{13}C NMR chemical shifts of **3a** and **3b** (**3c** and **3d**).

Scheme 3



	R^1	R^2	R^3		Yield (%)
1a	Me	H	Ph	**4a**	43
1b	Ph	Ph	Ph	**4b**	49
1a	Me	CO_2Me	CO_2Me	**4c**	23

To compare the photoreactivity of the analogous molybdenum and tungsten carbene complexes, we synthesized the corresponding compounds and extended the previous approach to their irradiation with alkenes. After 5 h of irradiation in hexane (for 0.25 mmol of **1c** or **1d** and 2.5 mmol of alkene), the reaction also occurs with formation of 1-pyrrolines **3** (Scheme 2). It is noteworthy to point out that molybdenum and tungsten carbenes can participate in the [3 + 2] cyclopentannulation process in a way similar to that for chromium. The greater reaction time required for molybdenum and tungsten complexes in comparison to their chromium analogues indicates a lower reactivity for the former metal carbenes in this photoreaction.

Next, we were interested in the photochemical behavior of complexes **1** in the presence of alkynes under the conditions described above. As shown in Scheme 3, the preliminary results indicate that light-induced reaction for acetylenes is analogous to that described for alkenes to give the 2*H*-pyrrole derivatives **4**. **4a** was the only detectable regioisomer in the crude reaction, and the configuration assignment was made by analogy to other 2*H*-pyrroles reported.[9]

In conclusion, we have reported that 3-aza-1-metalla-1,3-butadiene undergoes photochemical [3 + 2] cyclopentannulation with unsaturated systems instead of the expected benzannulation or cyclobutannulation reactions, providing a good method for the synthesis of 1-pyrroline and 2*H*-pyrrole derivatives. This is, as far as we know, the first time that such photochemical behavior has been observed. Furthermore, this photochemical reaction can be extended to molybdenum and tungsten carbene complexes. Experimental and theoretical studies to elucidate the mechanism and to extend the scope of this reaction are in progress.

Experimental Section

General Comments. All solvents were purified and dried by standard procedures and freshly distilled under dry Ar prior to use. ^{1}H and ^{13}C spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ with TMS as internal standard.

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Electrospray mass spectra were obtained on an HP 5989 B apparatus with an HP 59987 A interface, in negative-ion mode (for complexes **1**) or positive-ion mode (for compounds **2a**, **3**, and **4**). GC/MS spectra were recorded on an HP G1800A apparatus. IR spectra were obtained on a Perkin-Elmer 1000 spectrophotometer in CH_2Cl_2. Elemental analyses were performed using a CE Instrument, Model 1110. Reagents were of commercial grades (Aldrich).

Preparation of $(CO)_5Cr{=}C(Me)N{=}CPh_2$ (1a). The procedure to prepare **1a** is related to other nucleophilic attacks at Fischer carbene complexes.[7] (Methoxymethylcarbene)pentacarbonylchromium(0) (1.25 g, 5 mmol) and benzophenone imine (1.0 g, 5.5 mmol) were combined in deoxygenated Et_2O (20 mL). The mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum to give a red oil. Purification by column chromatography (silica gel, hexane/CH_2Cl_2 5:1) gave **1a** as a red solid. Yield: 1.84 g, 92%. Mp: 103−105 °C (lit.[7] mp 106 °C). ^{1}H NMR: δ 2.76 (s, 3H), 7.54 (bs, 10H). ^{13}C NMR: δ 35.1, 122.5, 128.3, 129.2, 130.1, 130.5, 208.3, 217.3, 223.3. IR: ν 2054 (m), 1974 (sh), 1928 (vs), 1508 (w), 1256 (m) cm^{-1}. ES: *m*/*z* 398 (M − 1). Anal. Calcd for $C_{20}H_{13}CrNO_5$: C, 60.16; H, 3.28; N, 3.51. Found: C, 60.01; H, 3.25; N, 3.53.

1b. Complex **1b** was prepared, as a red solid, in a way similar to that for **1a**, starting from (methoxyphenylcarbene)-pentacarbonylchromium(0) (1.56 g, 5 mmol). Yield: 1.85 g, 80%. Mp: 114−116 °C. ^{1}H NMR: δ 7.40−7.60 (m, 15H). ^{13}C NMR: δ 123.1, 125.9, 127.1, 128.4, 128.9, 129.2, 129.8, 131.3, 141.1, 210.8, 217.3, 223.6. IR: ν 2052 (m), 1976 (sh), 1926 (vs), 1506 (w), 1243 (m) cm^{-1}. ES: *m*/*z* 460 (M − 1). Anal. Calcd for $C_{25}H_{15}CrNO_5$: C, 65.08; H, 3.28; N, 3.04. Found: C, 64.98; H, 3.23; N, 3.08.

1c. Complex **1c** was prepared, as a red solid, in a way similar to that for **1a**, starting from (methoxymethylcarbene)-pentacarbonylmolybdenum(0) (1.47 g, 5 mmol). Yield: 1.38 g, 52%. Mp: 84−86 °C. ^{1}H NMR: δ 2.88 (s, 3H), 7.54 (bs, 10H). ^{13}C NMR: δ 36.9, 123.1, 129.2, 129.3, 130.0, 131.3, 189.6, 198.4, 203.1. IR ν 2059 (m), 1973 (sh), 1916 (vs), 1234 (m) cm^{-1}. ES: *m*/*z* 530 (M − 1). Anal. Calcd for $C_{20}H_{13}MoNO_5$: C, 54.19; H, 2.96; N, 3,16. Found: C, 54.10; H, 2.90; N, 3.14.

1d. Complex **1d** was prepared, as a red solid, in a way similar to that for **1a**, starting from (methoxymethylcarbene)-pentacarbonyltungsten(0) (1.91 g, 5 mmol). Yield: 2.02 g, 91%. Mp: 110−112 °C. ^{1}H NMR: δ 2.76 (s, 3H), 7.46 (s, 10H). ^{13}C NMR: δ 35.0, 119.8, 129.1, 129.2, 130.5, 130.9, 201.0, 206.2, 213.5. IR: ν 2063 (w), 1982 (vs), 1935 (vs), 1730 (w), 1509 (w), 593 (m) cm^{-1}. ES: *m*/*z* 442 (M − 1). Anal. Calcd for $C_{20}H_{13}WNO_5$: C, 45.22; H, 2.47; N, 2.64. Found: C, 45.25; H, 2.46; N, 2.67.

Irradiation Procedure. The carbene complex **1** (0.25 mmol) was disolved in 50 mL of deoxygenated hexane. Ten equivalents of the unsaturated compound was added, and the mixture was irradiated at room temperature under an Ar atmosphere, through Pyrex glass with a 125 W medium-pressure mercury lamp, until the carbene was consumed (TLC, hexane/CH_2Cl_2 1:1). The solvent was removed with a rotary evaporator, and the crude product was filtered through Celite to remove chromium residues. The product was purified by column chromatography (aluminum oxide, neutral, hexane/Et_2O 1:1).

Data for 2a. Compound **2a** was obtained when the unsaturated compound was not added. Yield: 23 mg, 25%. ^{1}H NMR: δ 1.87 (s, 3H), 6.70−7.60 (m, 20H). ^{13}C NMR: δ 21.3, 121.7, 125.1, 126.2, 127.4, 127.5, 127.7, 127.9, 128.1, 128.5, 128.9, 129.0, 130.2, 130.6, 137.0,139.0, 141.4, 142.4, 144.1, 166.0. IR: ν 3682 (w), 3600 (w), 3026 (m), 2924 (m), 1713 (m), 1620 (s), 1596 (s), 1492 (s), 1444 (s), 1316 (m) cm^{-1}. ES: *m*/*z* 374 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 373 (M, 5), 358 (3), 296 (6), 165 (100), 139 (15), 115 (26) 91 (18), 77 (22), 51 (20). Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.23; N, 3.63.

Data for 3a. Yield: 41 mg, 54%. ^{1}H NMR: δ 0.83 (t, 3H), 2.17 (s, 3H), 2.75 (dd, J = 9.3, 17.6 Hz, 1H), 3.19 (dd, J = 6, 17.6 Hz, 1H), 3.4−3.6 (m, 2H), 3.95 (dd, J = 6, 9.3 Hz, 1H), 6.9−7.6 (m, 10H). ^{13}C NMR: δ 13.6, 19.6, 42.9, 52.9, 60.7, 87.8, 126.8, 126.9, 127.3, 127.5, 127.7, 128.1, 143.0, 145.9, 172.3, 172.8. IR: ν 1713 (s), 1654 (m) cm^{-1}. ES: *m*/*z* 308 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 307 (M, 7), 234 (85), 220 (14), 165 (100), 139 (12), 115 (35), 104 (42), 91 (61), 77 (52), 53 (65). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.17; H, 6.84; N, 4.59.

Data for 3b. Yield: 53 mg, 76%. ^{1}H NMR: δ 1.56 (s, 3H), 2.22 (s, 3H), 2.72 (dd, J = 8.4, 17.4 Hz, 1H), 3.08 (dd, J = 4.2, 17.4 Hz, 1H), 4.13 (dd, J = 4.2, 8.4 Hz, 1H), 7.00−7.60 (m, 10H). ^{13}C NMR: δ 19.6, 29.9, 42.6, 59.4, 87.0, 127.1, 127.1, 127.4, 127.7, 128.0, 128.3, 143.2, 145.4. IR: ν 1707 (s), 1656 (m) cm^{-1}. ES: *m*/*z* 278 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 277 (M, 3), 234 (16), 207 (18), 182 (19), 165 (100), 139 (15), 115 (23), 96 (19), 77 (31), 51 (35). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.32; H, 6.88; N, 5.15.

Data for 3c. Yield: 16 mg, 21%. ^{1}H NMR: δ 2.23 (s, 3H), 2.75 (dd, J = 6,9 Hz, 1H), 3.02 (dd, J = 6, 9 Hz, 1H), 4.28 (dd, J = 6, 6 Hz, 1H), 6.67 (m, 2H), 6.82 (m, 2H), 6.95 (m, 4H), 7.1−7.6 (m, 5H), 7.57 (m, 2H). ^{13}C NMR: δ 20.1, 48.4, 53.3, 89.5, 126.1, 126.6, 127.2, 127.7, 128.1, 128.9, 141.6, 143.4, 171.4. ES: *m*/*z* 312 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 311 (M, 3), 270 (4), 207 (43), 165 (100), 139 (15), 115 (14), 104 (18), 77 (15), 51 (11). Anal. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.65; H, 6.86; N, 4.49.

Data for 3d. Yield: 52 mg, 61%. ^{1}H NMR: δ 1.62 (s, 3H), 3.16 (dd, J = 6,7.5 Hz, 1H), 3.59 (dd, J = 6, 7.5 Hz, 1H), 4.25 (dd, J = 6, 6 Hz, 1H), 7.2−8.0 (m, 15H). ^{13}C NMR: δ 29.5, 38.7, 59.9, 87.0, 127.5, 127.7, 128.3, 128.7, 130.1, 130.9, 131.7, 132.4, 133.8, 141.4, 143.3, 145.7, 170.7, 208.2. ES: *m*/*z* 340 (M + 1). Anal. Calcd for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.97; H, 6.26; N, 4.07.

Data for 4a. Yield: 33 mg, 43%. ^{1}H NMR: δ 2.38 (s, 3H), 6.77 (s, 1H), 7.22−7.36 (m, 10H). ^{13}C NMR: δ 18.9, 90.4, 126.2, 126.9, 127.2, 127.5, 127.8, 127.9, 128.1, 128.3, 128.4, 128.6, 128.7, 133.5, 139.3, 170.7. IR: ν 3684 (w), 3058 (m), 1684 (w), 1619 (m), 1599 (m), 1492 (m) cm^{-1}. ES: *m*/*z* 310 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 309 (M, 28), 265 (5), 230 (8), 191 (15), 165 (100), 139 (12), 102 (72), 77 (92), 51 (95). Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.34; H, 6.15; N, 4.51.

Data for 4b. Yield: 55 mg, 49%. ^{1}H NMR: δ 6.95−7.88 (m, 25H). ^{13}C NMR: δ 92.15, 119.1, 123.5, 125.5, 126.4, 126.5, 127.5, 127.7, 127.8, 128.0, 128.2, 128.3, 128.6, 128.7, 131.2, 132.4, 135.5, 136.7, 138.6, 140.8, 141.2, 147.4, 148.2, 170.1. IR: ν 3053 (m), 1712 (s), 1626 (m), 1596 (m), 1577 (m), 1492 (m), 1447 (m) cm^{-1}. ES: *m*/*z* 448 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 447 (M, 15), 370 (8), 292 (27), 252 (23), 165 (100), 139 (16), 103 (15), 77 (79), 51 (63). Anal. Calcd for $C_{34}H_{25}N$: C, 91.24; H, 5.63; N, 3.13. Found: C, 91.20; H, 5.61; N, 3.19.

Data for 4c. Yield: 20 mg, 23%. ^{1}H NMR: δ 2.47 (s, 3H), 3.69 (s, 3H), 3.88 (s, 3H), 7.1−7.4 (m, 10H). ^{13}C NMR: δ 18.3, 52.4, 52.6, 92.3, 127.9, 128.0,128.1, 128.1, 128.2, 128.3, 134.3, 135.6, 138.2, 163.2, 163.5, 163.7, 167.9. IR: ν 3680(w), 1737-(s), 1728(s), 1639 (m) cm^{-1}. ES: *m*/*z* 350 (M + 1). GC/MS: *m*/*z* (relative intensity, %) 349 (M, 43), 258 (35), 230 (29), 189 (28), 165 (10), 127 (56), 102 (15), 77 (39), 59 (100). Anal. Calcd for $C_{26}H_{21}NO_4$: C, 75.90; H, 5.14; N, 3.40. Found: C, 75.98; H, 5.16; N, 3.39.

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