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Michael Addition of Chiral Fischer Aminocarbene Complexes to Nitroolefins: Study on the Effect of the Michael Acceptor Structure on Diastereoselectivity

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The anions of the pentacarbonyl(chromium) *trans*-2,6-dimethylmorpholinyl(methyl)carbene and pentacarbonyl(chromium) *trans*-3,5-dimethylpiperidinyl(methyl)carbene complexes added to *E*- and *Z*-nitrostyrenes through a diastereoselective Michael-type reaction to give precursors of β-aryl-γ-butyric acid derivatives. The diastereoselectivity observed with the former carbene was dependent on the nature of the substituent present in the 4-position of nitrostyrenes and was higher when it was an electron-withdrawing group. The presence of 12-crown-4 ether in the reaction medium increased both reaction times and diastereoselectivity. Theoretical calculations were performed to rationalize the stereochemical outcomes of the reactions and to support the proposed transition state models.

Introduction

The synthetic potential of Fischer-type carbene complexes in the formation of new carbon−carbon bonds is well documented by a host of publications.[1] A widely used general synthetic strategy consists of the addition of the carbanion α to the carbene carbon to electrophilic reagents.

Recently, anions of chiral amino carbene complexes have been successfully used in Michael addition reactions to enones.[2] These reactions give δ-keto carbene complexes with good to high levels of diastereoselectivity.

We have recently reported[3] the first example of addition of Fischer carbene anions to nitroalkenes. These anions effectively delocalize the negative charge into the $Cr(CO)_5$ group, and they are stabilized and soft enough to become suitable nucleophiles toward powerful but base-sensitive reagents such as nitroolefins.[4] Our previous results[3] indicate that the anion of pentacarbonyl(chromium) *trans*-2,6-dimethylmorpholinyl(methyl)carbene complex **1** undergoes Michael addition to nitroalkenes **5a**,**b**,**k**,**l** (Chart 1). The adducts are diastereomeric enriched mixtures. An interesting result of those reactions is that the de value is increased from 30% to 50% by replacement of nitrostyrene with *p*-chloronitrostyrene. We therefore decided to investigate further whether the nature of the substituent present on the nitroolefin arene ring effects de values.

Results

Herein we report our new results on the extension of Michael additions of **1** and its piperidino analogue **2** to a series of differently aryl-substituted *E*- and *Z*-nitroalkenes. The synthesis of complexes **1** and **2** was perfomed by the aminolysis reaction of pentacarbonylmethoxy (methyl)carbene chromium with *trans*-(±)-2,6-dimethylmorpholine[2b] and *trans*-(±)-3,5-dimethylpiperidine, respectively. A single crystal of complex **1** was submitted to X-ray analysis. An ORTEP plot of compound **1** is given in Figure 1, while selected bond lengths and angles are listed in Table 1.

The immediate coordination sphere around the Cr atom consists of five CO ligands and the aminocarbene moiety. The bond lengths and angles are unexceptional and fall in the expected range[5] for this class of com-

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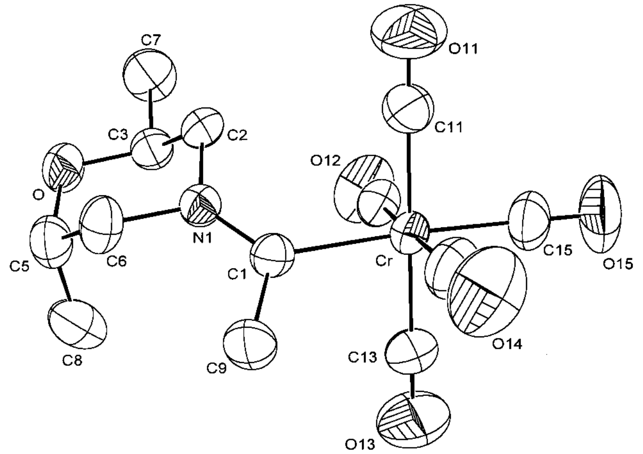
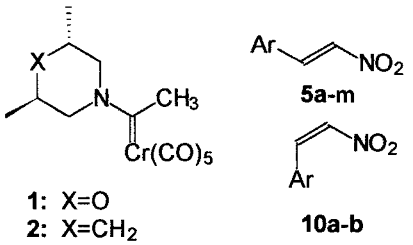


Figure 1. ORTEP view of compound **1.** Thermal ellipsoids drawn at 50% probability.

Chart 1



1: X=O
2: $X=CH_2$
5a-m
10a-b

	Ar		Ar
a	Ph	**h**	*m*-NO_2-Ph
b	*p*-Cl-Ph	**i**	$[(CO)_3Cr]\eta^6$-Ph
c	*p*-NO_2-Ph	**j**	$[(CO)_3Cr]\eta^6$-*p*-Cl-Ph
d	*p*-Me-Ph	**k**	Fur
e	*p*-MeO-Ph	**l**	Th
f	*p*-Me_2N-Ph	**m**	Py
g	*o*-NO_2-Ph		

pounds. For example, the Cr–C1 and C1–N1 separations at 2.127(3) and 1.308(4) Å, respectively, are identical with those reported for the complex $Cr(CO)_5$-(methylthiazolidine)[6] (2.123(3) and 1.300(4) Å, respectively).

The Cr–CO distances are similar and comparable with those in ref 6 and show a Cr–CO bond *trans* to the carbenic moiety slightly shorter than the others.

The conformation of complex **1** is best described by the dihedral angles (see Table 1), e.g., Cr–C1–N1–C6, 179.9(3)°, C6–N1–C1–C9, 0.2(5)°, and C14–Cr–C1–C9, −44.1(3)°, which show the relative orientation of the carbene ligand with respect to the $Cr(CO)_5$ moiety.

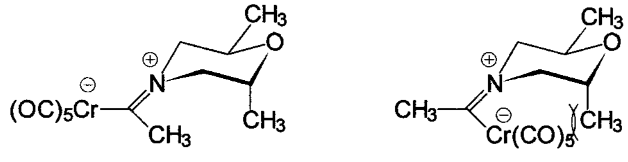
Table 1. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Compound 1

Cr–C1	2.127 (3)	C1–Cr–C15	175.4 (2)
N1–C1	1.308 (4)	C11–Cr–C13	180.0 (5)
Cr–C11	1.890 (4)	C12–Cr–C14	176.9 (2)
Cr–C12	1.871 (4)	Cr–C1–N1	129.5 (2)
Cr–C13	1.882 (4)	Cr–C1–C9	116.8 (2)
Cr–C14	1.889 (4)	N1–C1–C9	113.7 (3)
Cr–C15	1.860 (4)		
C–O[a]	1.141(9)		

Cr–C1–N1–C6	179.9 (3)
Cr–C1–N1–C2	5.9 (4)
C6–N1–C1–C9	0.2 (5)
C14–Cr–C1– N1	136.3 (3)
C14–Cr–C1–C9	−44.1 (3)

[a] Average value.

Chart 2



rotamer 1A **rotamer 1B**

Moreover, from the structure in Figure 1 it can be inferred that complex **1** exists, in the solid state, as the conformer in which the axial methyl group (C8) on the six-membered ring is opposite the $Cr(CO)_5$ group with respect to the C1–N1 double bond. The same conformation for complex **1** was found in solution, and in the ^1H NMR time scale, a single, stable, conformationally rigid rotamer was observed (Chart 2). The explanation could be that the six-membered ring flipping is prevented by the presence of the bulky substituent on the nitrogen atom [the $Cr(CO)_5CCH_3$ group], which renders the half-chair intermediate of the ring-flipping process a high-energy species. In this situation two distinct rotamers should be expected, one with the axial methyl substituent opposite the $Cr(CO)_5$ (rotamer **1A**) and the other one with the axial methyl group on the same side of the Cr-$(CO)_5$ moiety (rotamer **1B**). Clearly, rotamer **1A** is more stable than **1B** and is the one present both in the solid state and in solution. A dynamic ^1H NMR spectrum of complex **1** in deuterated nitrobenzene shows a broadening of the signals at 60 °C, thus indicating the ring-flipping process at this temperature.

The Michael-type addition of the anion **3**, generated by deprotonation of carbene **1** with *n*-BuLi at −78 °C, to (*E*)-nitroalkenes **5a**–**m** in THF at − 78 °C afforded the diastereomeric addition products **6a**–**m** and **7a**–**m** (see Scheme 1). All of the reactions were run at an initial concentration of **1** of 0.020 M. Reaction times, yields, and de ratios are listed in Table 2. The two diastereoisomers **6** and **7** were easily separated and obtained as pure complexes by flash column chromatography.

The configuration was previously demonstrated by X-ray analysis[3] to be (*R*,*R*,*S*)-(*S*,*S*,*R*) for compound **6b**, the major diastereomer of the addition reaction of **3** to *p*-chloronitrostyrene. Correlations between ^1H NMR signals of the same type allowed us to assign easily the configuration to analogue products **6a**–**d**,**g**–**j**,**m**. Moreover, we found that in the major isomer **6b** the two diastereotopic hydrogen atoms of the CH_2NO_2 group are isochronous and exhibited an upfield doublet; while a

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Scheme 1. Michael Addition of Carbene Complexes 1 and 2 to *E*-Nitroolefins

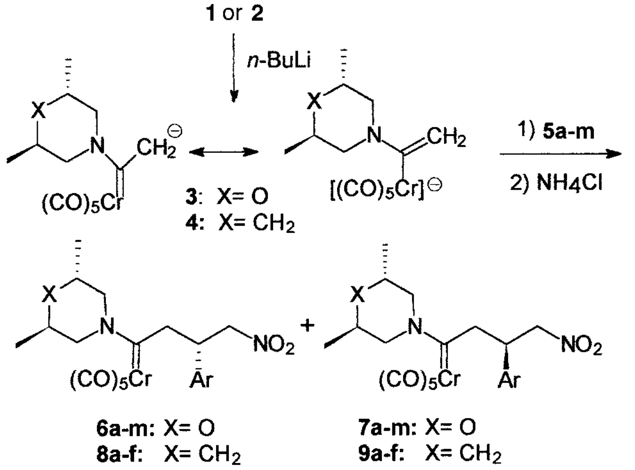
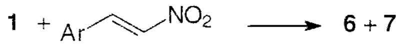


Table 2. Substituent Effect in the Michael Addition of Carbene 1[a] to Nitroalkenes



entry	prod **6**+**7**	time[b] (min)	yield (%)	**1**[c] (%)	de[d] (%)
1	**a**	30	85	9	30
2	**b**	25	80	16	50
3	**c**	40	74	21	69
4	**d**	60	81	17	22
5	**e**	80	68	28	6
6	**f**	240	66	10	37
7	**g**	75	72	13	29
8	**h**	45	52	32	55
9	**i**	75	72	23	77
10	**j**	25	82	16	66
11	**k**	40	91	7	40
12	**l**	30	91	6	20
13	**m**	1200	38	60	71[e]

[a] Initial concentration of **1**: 0.02 M. [b] Time is calculated from the end of addition of nitroalkene that is completed in 20 min. [c] **1** recovered after workup. [d] The major diastereomer was (*R*,*R*,*S*)-(*S*,*S*,*R*) for all the reactions except for entries 5 and 6, which was (*R*,*R*,*R*)-(*S*,*S*,*S*). [e] Calculated on isolated mix of adducts.

second-order signal with eight lines was present downfield in the minor diastereoisomer **7b** (see Figure 2, A). Furthermore, the methyl substituents of the 2,6-dimethyl morpholinyl group appeared as two distinct doublets. The more downfield signal belonged to the equatorial methyl group and the more upfield to the axial one (Figure 2, B). This trend has been found in all of the couples of diastereomers (**6a**−**d**,**g**−**j**,**m**), thus allowing the assignment of their relative configurations.

We were able to assign the (*R*,*R*,*R*)-(*S*,*S*,*S*) configuration in the same way to the major adducts **7e**,**f** obtained from the reactions of **3** with *p*-methoxy- or *p*-(dimethylamino)nitrostyrenes **5e** and **5f** and to the major adducts **7k** and **7l** obtained with electron-rich heteroaryl derivatives **5k** and **5l**, where the previous minor diastereoisomer became the major one.

The results of this study shown in Table 2 were in some way unexpected and of significance. When the substituent is in the *para* position on the aromatic ring, the diastereomeric excess of the addition reaction seems to be influenced by the electronic character of the substituents: it is quite low for nitrostyrene itself (de 30%, entry 1) and higher for chlorine (de 50%, entry 2), whereas the highest de's of 69 and 77% (entries 3 and 9) were found for the electron-withdrawing nitro and chromium tricarbonyl units.

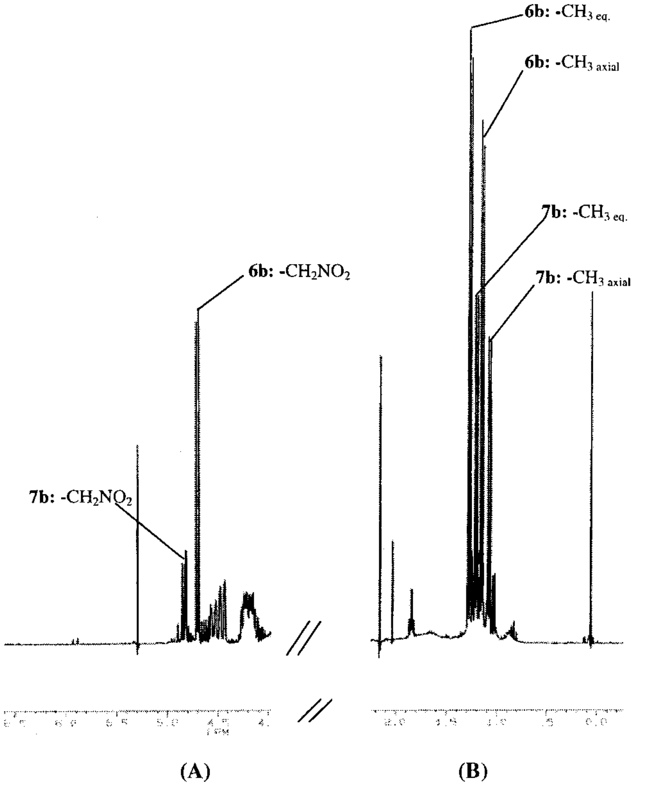


Figure 2. ^1H NMR regions of CH_2NO_2 (A) and CH_3 (B) signals for compounds **6b** and **7b**.

Ortho- and *meta*-nitro-substituted nitrostyrenes **5g** and **5h** showed lower de values, probably because, at least in the case of the *ortho* derivative **5g**, of unfavorable steric effects. On the contrary, the diastereoselectivity decreased when electron-donating substituents were present in the *para* position (nitroalkenes **5d**−**f**), such as 22% for *p*-methyl-substituted nitroalkene **5d** (entry 4), 6% for *p*-methoxyl **5e** (entry 5), and 37% for *p*-dimethylamino **5f** (entry 6). Moreover, we observed an inversion in diastereoselectivity, and the opposite diastereoisomer (*R*,*R*,*R*,)-(*S*,*S*,*S*) was in the latter two cases the major one.

Nitroolefins with an electron-rich heteroaryl substituent such as furyl and thienyl derivatives **5k**,**l** (Table 2, entries 11 and 12) showed a de of 40% and 20%, respectively, which are lower than those observed with electron-poor aryl groups. In both classes, however, the major diastereoisomers held the (*R*,*R*,*S*)-(*S*,*S*,*R*) configuration.[7]

As shown in Table 2, the reaction rate of Michael addition was found lower for nitrostyrenes substituted by donor groups. These results can be explained by the kinetics of addition of anion **3** to substituted nitrostyrenes. The rates depended on the different electronic characteristics of the *para*-substituent. Bernasconi et al.[8] reported that π-donor substituents, such as *p*-methoxy or *p*-dimethylamino groups, show deviation

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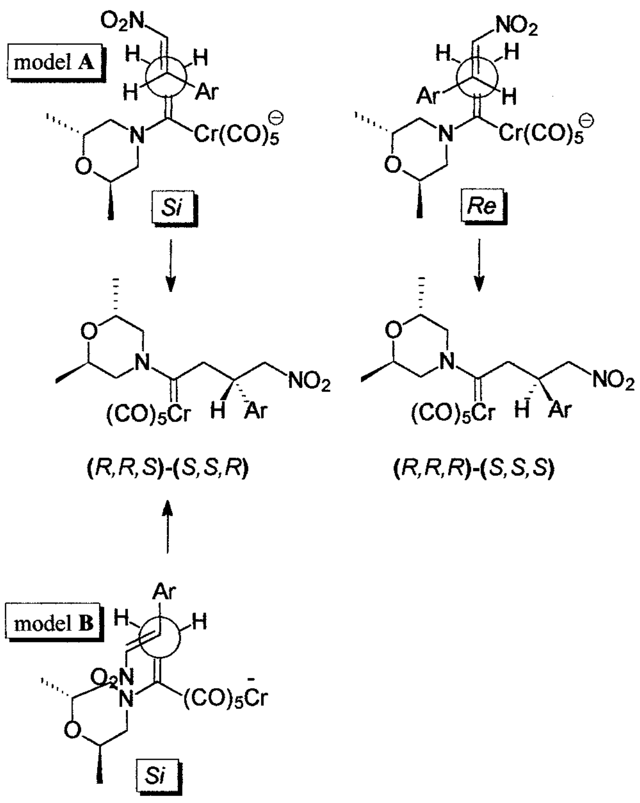
(7) We tried also other electron-poor nitroalkenes: (nitro-2-ethenyl)-5-nitrofurane and (nitro-2-ethenyl)-5-nitrothiophene. Unfortunately both reagents and products were very sensitive to the reaction and the workup conditions, and products could not be isolated and properly characterized.

Chart 3



from Hammett or Brønsted plots in the addition of hydroxide and nitromethide ion to substituted β-nitrostyrenes.

The results so far found, concerning carbene **1**, led us to form hypotheses about the stereochemistry of attack of anion **3** to nitroalkenes. In our previous paper[3] we discussed as a suitable model of attack the one reported by Seebach[9a] and more recently utilized by Mülzer[9b] (model **B**, Chart 3), where in the transition state, the nitro group should be oriented near the nitrogen atom of the amino group. The deeper study we report in this paper better accounts for the transition state model **A** represented in Chart 3.

In this model, the *si* face of the EWG-substituted nitrostyrene reacts with the anion **3** with the aryl group facing the negatively charged $Cr(CO)_5^-$ moiety because of a favorable electronic interaction. The resultant transition state leads to the major diastereoisomer *(R,R,S)-(S,S,R)*. Donor groups present on the aryl ring should render such kind of interaction less probable. Consequently, the aryl group would be far away from $Cr(CO)_5^-$, as shown in Chart 3, in which the *re* face of the nitroolefins reacts with carbene anion **3** to give minor diastereoisomer (*R,R,R*)-(*S,S,S*). Both models **A** and **B** could justify the stereochemistry of the major diastereoisomer obtained with EWG-substituted nitrostyrenes. However, model **B** does not explain variations of the de value with the electronic characteristics of the substituent nor the inversion of configuration observed in reactions with EDG-substituted nitrostyrenes **5e**,**f**. On the contrary, the model **A** seems consistent with both of these stereochemical outcomes of the addition reactions.

Chart 4

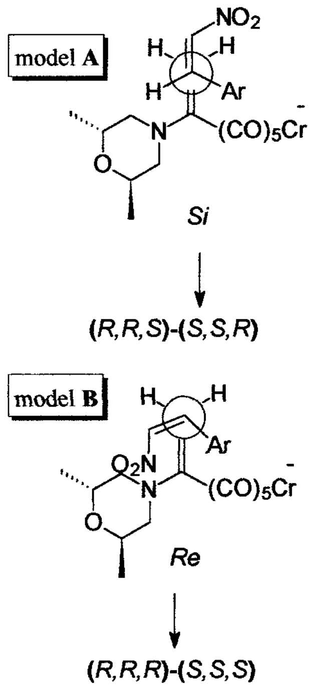
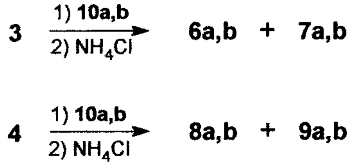


Table 3. *Z*-Alkenes in the Michael Addition of Carbenes 1 and 2[a]

entry	A[b]	P[c]	time (min)	yield (%)	**1** or **2**[d] (%)	de[e] (%)
1	**10a**	**6a, 7a**	120	65	**1** (30)	58
2	**10b**	**6b, 7b**	200	67	**1** (21)	83
3	**10a**	**8a, 9a**	20	66	**2** (20)	73
4	**10b**	**8b, 9b**	30	80	**2** (16)	90

[a] Initial concentration of **1** (or **2**); 0.02 M. [b]A = alkene. [c]P = products. [d]Recovered at the end of reaction. [e]In each case the major diastereomer was (*R,R,S*)-(*S,S,R*).

Scheme 2. Michael Addition of Complex Anions 3 and 4 to *Z*-Nitroolefins



Besides this, we thought that if model **B** operates, the use of a *Z*-nitroalkene should have led to an inversion of configuration of the major diastereomer with respect to that obtained with the corresponding *E*-nitroalkene, whereas model **A** (Chart 4) should have afforded adducts with the same configuration.

Our results listed in Table 3 involving *Z*-nitroalkenes (Scheme 2) show that the configuration of the major diastereomer was the same as that obtained with the corresponding *E*-alkenes. Moreover, the percent of de was higher than those obtained with the isomeric *E*-**5a**,**b**, (i.e., 58% and 83%, respectively).

These results are of significance from a synthetic point of view and again could be explained by the transition state model **A**. An electronic interaction could exist in this process between the aromatic ring and $Cr(CO)_5^-$ moiety. Moreover, the gain in de values

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passing from *E*- to *Z*-nitroolefins could also be explained by steric reasons. In fact, as already reported in the literature,[10] *Z* aryl nitroolefins do not have a planar configuration, and this fact leads to a less crowded transition state, as also shown by molecular models.

To support this hypothesis, we performed some calculations and molecular modeling.

The Builder and Discover modules of Insight II from Biosym Technologies were used for model building and energy minimization, respectively. The energies for all conformations were minimized with the extensible systematic forcefield calculation (ESFF) until the maximum derivative was less than 0.001 kcal/(mol Å). All of the calculations were carried out by use of a Silicon Graphics workstation.

The input of two pairs of starting materials is shown in Figure 3a, which includes the carbene anion **3** approaching *E*-nitrostyrene (**5a**) from the *si* face (on the left) and the *re* face (on the right, cf. Chart 3). We place carbene anion **3** in front of *E*-nitrostyrene (**5a**) for a better view.

The output is shown in Figure 3b, which resulted from energy minimization by ESFF calculations. The electron cloud showed the possibility of π-stacking. For *E*-nitrostyrene (**5a**) with the *si* face shown on the left side, π-stacking clearly existed between two carbonyl groups attached to the Cr atom and the benzene ring in **5a**. In contrast, it did not exist in the matrix involving the *re* face shown on the right side. We also found that the minimized energy was lower for the *si* matrix than the *re* matrix by 1.324 kcal/mol.

We summarize the computational results on energy in Table 4.

The data were obtained from many calculations related to eight pairs of complexes containing the morpholino-substituted carbene anion **3** and a *E*-nitrostyrene (**5**) with the *si* or the *re* face. Each of them is associated with similar figures, as shown in Figure 3a,b. We found that six of the eight pairs showed lower energy for the approach involving the *si* face than the *re* face; the ΔE ($=E_{si} - E_{re}$) values were negative. Only nitrostyrenes **5e**,**f**, both possessing an EDG-substituent, gave positive ΔE values. These computational results are consistent with the outcomes from experiments shown in Table 2. The major products isolated by use of **5e**,**f** as the starting materials possessed the configuration (*R*,*R*,*R*)-(*S*,*S*,*S*) instead of (*R*,*R*,*S*)-(*S*,*S*,*R*) resulting from the other six pairs.

The final products resulting from the *si* and the *re* faces had very close energies (<0.023 kcal/mol). An example is shown in Figure 3c, in which the ΔE is 0.013 kcal/mol for the diastereomeric products **6a** and **7a.** Therefore the selectivity does not come from thermodynamic control. We believe that the possibility of π-stacking leads to the selectivity.

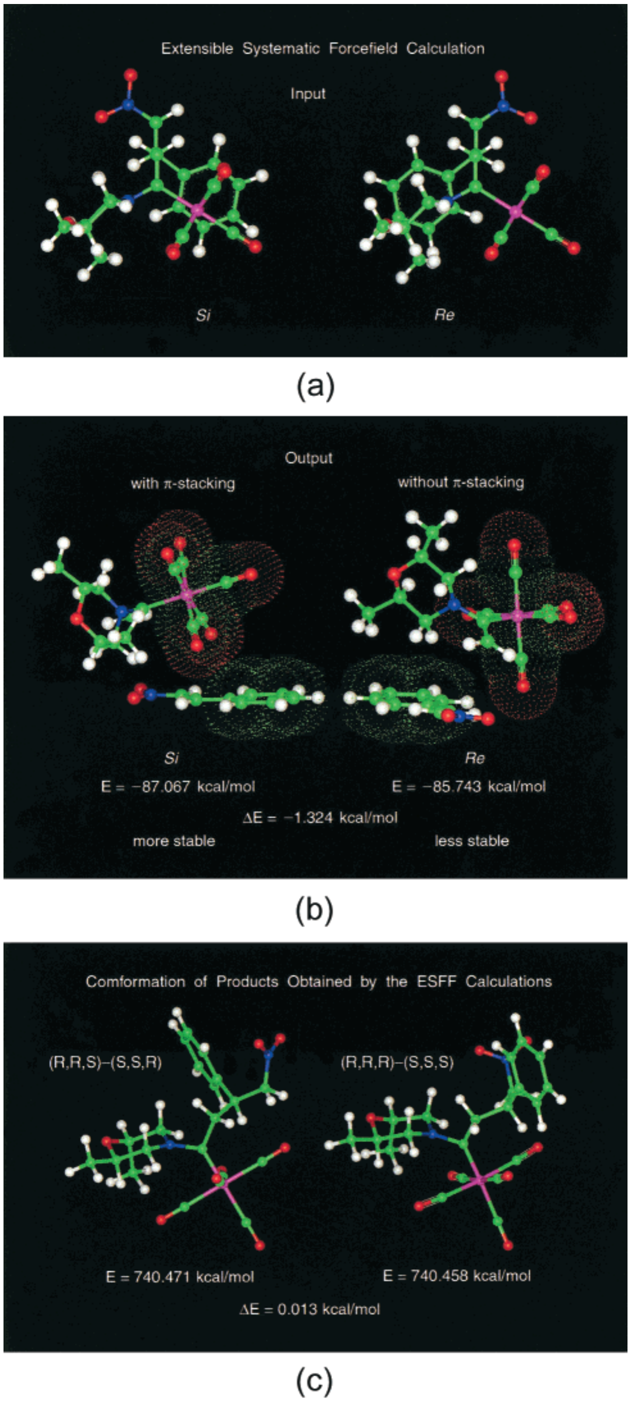

Figure 3. (a) Input of two pairs of starting materials including the *si* face (on the left) and the *re* face (on the right) of *trans*-nitrostyrene **5a** with the carbene anion **3**, which is placed in front. (b) Output after energy minimization by ESFF calculations. The electron cloud shows the possibility of π-stacking. (c) Conformation and energies of the final products **6a** and **7a**, generated from the *si* and *re* faces, respectively.

Recently, Venzo et al.[11] have reported the first experimental evidence of both intra- and intermolecular attractive electron interactions between the C≡O orbitals of the tricarbonylchromium fragment in arene tricarbonylchromium complexes and the π-system of an aromatic ring. These interactions are described as "unconventional bond interactions of charge-transfer bonding type, in which donor−acceptor energy or polarization energy or both does exceed the Van der Waals repulsion energy".

These rationales, together with our calculation results, support the hypothesis of an attractive interaction

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[10] Miller, D. B.; Flanagan, P. W.; Shechter, H. *J. Org. Chem.* **1976**, *41*, 2112−2120.

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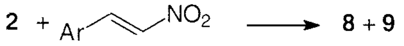
Table 4. Energies Obtained by ESFF Calculations for the Complex Containing Morpholino-Substituted Carbene Anion 3 and a *trans*-Nitrostyrene (*trans*-ArCH=CHNO$_2$, 5) with the *si* Face or the *re* Face

5	Ar	E_{si}[a]	E_{re}[a]	ΔE[a] (=$E_{si} - E_{re}$)
a	Ph	−87.067	−85.743	−1.324
b	*p*-ClPh	−87.227	−86.219	−1.008
c	*p*-NO$_2$Ph	−83.110	−81.085	−2.025
d	*p*-MePh	−87.748	−87.029	−0.719
e	*p*-MeOPh	−88.464	−88.679	0.215
f	*p*-Me$_2$NPh	−95.031	−95.672	0.641
k	2-furyl	−102.316	−101.744	−0.572
l	2-thienyl	−96.453	−95.192	−1.261

Table 5. Substituent Effect in the Michael Addition of Carbene 2[a] to Nitroalkenes



entry	prod **8** + **9**	time[b] (h)	yield (%)	**2**[c] (%)	de[d] (%)
1	**a**	6	71	25	42[e]
2	**b**	5.5	74	20	46
3	**c**	5	53	25	40
4	**e**	2.3	80	10	8[d]
5	**f**	20		80	
6	**f**	2	69	9	44[d]

[a] Initial concentration of **2**: 0.02 M, except for entry 6, for which it was 0.2 M. [b] Time is calculated from the end of addition of nitroalkene that is completed in 20 min. [c] **2** recovered after workup. [d] The major diastereomer was (*R*,*R*,*S*)-(*S*,*S*,*R*) for all the reactions except for entries 4 and 6, for which it was (*R*,*R*,*R*)-(*S*,*S*,*S*). [e] 44% in ^{13}C NMR spectrum.

Table 6. Michael Addition at Different Concentrations of Complex 1

entry	**A**[a]	**C**[b] (mol/L)	time (min)	yield (%)	**1**[c] (%)	de[d] (%)
1	**5a**	0.0205	30	86	9	30
2	**5a**	0.08	20	75	18	18
3	**5a**	0.22	35	66	24	28
4	**5b**	0.002	20		100	
5	**5b**	0.0205	25	80	16	50
6	**5b**	0.067	20	60	36	35
7	**5b**	0.22	20	67	20	58
8	**5k**	0.0205	40	91	7	40
9	**5k**	0.22	40	82	12	24
10	**5l**	0.0205	30	91	6	20
11	**5l**	0.22	30	67	25	13

[a] A = alkene. [b] Initial concentration of **1**. [c] Recovered at the end of reaction. [d] In each case the major diastereomer was (*R*,*R*,*S*)-(*S*,*S*,*R*).

Table 7. Use of 12-Crown-4 Ether in Michael Addition of 1 to *E*-Nitroalkenes 5a−c,e,f,i[a]

entry	prod **6** + **7**	time (h)	yield (%)	**1**[b] (%)	de[c] (%)
1	**a**	4.3	80	19	65
2	**b**	4.3	67	38	80
3	**c**	22	4	48	
4	**c**	3.0	58	30	68
5	**e**	21	23	64	33
6	**e**	4.5	62	36	24
7	**f**	20	41	31	42
8	**i**	5.5	53	40	10

[a] Initial concentration of **1**: 0.02 M except for entries 4 and 6, for which it was 0.20 M. [b] Recovered at the end of reaction. [c] In each case the major diastereomer was (*R*,*R*,*S*)-(*S*,*S*,*R*) except for entry 7, for which it was (*R*,*R*,*R*)-(*S*,*S*,*S*).

between two of the five CO ligands and the aromatic ring of the nitrostyrenes substituted with an electron-withdrawing group.

We then carried out the Michael-type addition to nitrostyrenes of the anion of the pentacarbonyl(chromium) *trans*-3,5-dimethylpiperidinyl(methyl)carbene **2**, a carbene complex in which the chiral auxiliary is *trans*-3,5-dimethyl piperidine (Chart 1, Scheme 1). The anion **4**, generated from **2**, was qualitatively found to react slower with nitroalkenes **5a**−**f** comparing with anion **3** (Scheme 1, Table 5). We found a similar behavior with regard to diastereoselectivity: the major adduct in reactions with **5a**−**c** was recognized to be **8a**−**c** [(*R*,*R*,*S*)-(*S*,*S*,*R*)],[12] but unexpectedly the de did not appear to be affected by the EWG-substituents in the *para* position of nitrostyrene. The de values were around 40% for hydrogen, *p*-Cl, or *p*-nitro substitued nitrostyrenes (Table 5, entries 1−3). With donor groups, the diastereoselectivity was reversed (Table 5, entries 4, 6), exactly as we found for reactions of carbene **1**, and the major diastereomer in these two cases was **9e**,**f** [(*R*,*R*,*R*)-(*S*,*S*,*S*)]. In the case of *p*-dimethylamino-substituted nitroalkene **5f**, it was necessary to use a more concentrated solution of the starting complex **2** (see Experimental Section, procedure B) for formation of the adduct (Table 5, entries 5, 6).

The stereochemical model we propose fits well with reactions of morpholinyl carbene **1**, although it does not act the same as piperidinyl carbene **2**. The reason is not clear yet. One of the possibilities is that anions **3** and **4** are present as aggregates in solution instead of a simple ion pair. The aggregation would occur more likely with **3** than **4** because of the presence of an oxygen atom in the morpholinyl ring. This oxygen atom together with a lithium cation could form a bridge between two identical structures to make dimers, trimers, tetramers, or polymers.[13] Moreover, this atom could participate in precomplexation with nitroalkene. The absence of the oxygen atom in the C_2-symmetric amine in anion **4** would lead to a different arrangement that would be less influenced by different types of nitroalkenes, which affects diastereoselectivity. Different Li$^+$-carbanion aggregates could also be responsible for the very different reaction rates of the two anions **3** and **4**.

The presence of Li$^+$ aggregates is supported by the fact that, carrying out the reaction of **1** at different concentrations, some variations in yields and diastereoselectivities were observed (Table 6). In addition, we performed the Michael addition reaction of anion **3** in the presence of crown ethers, which would allow the lithium cation to disassociate with the counteranion. Therefore, 12-crown-4 was added to the anion **3** solution prior to the nitroalkene addition. Chemical yields and diastereoselectivities were different from those of reactions without additives (see Table 7), and reaction rates were lower. Likely, lithium acts as a Lewis acid to the alkene nitro group, both enhancing its reactivity as a Michael acceptor and favoring its approach to the carbene anion, thus leading to a faster reaction.

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[12] Also in this case correlation of ^{1}H NMR was utilized to assign the relative configuration.

[13] (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624−1654. (b) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277−297. Enders, D.; Kirchhoff, J.; Gerdes, P.; Mannes, D.; Raabe, G.; Runsink, J.; Boche, G.; Marsch, M.; Ahlbrecht, H.; Sommer, H. *Eur. J. Org. Chem.* **1998**, 63−72.

Conclusions

Soft chiral carbene anions **3** and **4** easily react in a Michael-type addition to nitroolefins affording the expected adducts in good yields and from modest to good de. These adducts are precursors of β-aryl-γ-butyric acid derivatives, and we have already published an application of an enantioselective version of this chemistry to the synthesis of (*R*)-(−)-baclofen.[14]

In the present study we have pointed out that the diastereoselections in the Michael addition of the morpholinyl carbene anion **3** to nitrolefins are affected by (i) the nature of the substituent present in the *para* position of the arylnitroalkene; (ii) the nitroalkene double bond geometry; and (iii) the absence of the lithium cation. Higher diastereoselectivities are obtained when (i) electron-withdrawing substituents are present in the *para* position on the aromatic ring of the nitroalkene; (ii) nitroalkenes with a *Z* geometry of the double bond are used; (iii) a sequestering of the lithium cation such as 12-crown-4 ether is added to the reaction mixture.

The stereochemical outcome of reactions can be explained by considering the transition state model **A** reported in Chart 3, whose stabilization could arise from a favorable electronic interaction between the negatively charged $Cr(CO)_5^-$ group and the electron-poor aromatic ring of the nitroalkene. This hypothesis is supported by theoretical calculations, which show the possibility of a π-stacking interaction between two of the five CO ligands and the electronic cloud of the aromatic ring. A recent literature report also supports this possibility.[11]

Experimental Section

General Comments. All the reactions were carried out under nitrogen atmosphere, and the solvents were dried by distillation over sodium wires. Nitroalkenes were commercially available or prepared by simple procedures reported in the literature, except for (*Z*)-*p*-chloro-β-nitro-styrene.[15]

Morpholinyl chromium carbene **1** was prepared as reported.[2b] Buthyllithium solutions were titrated before use. Flash and vacuum chromatography was performed with Silica Gel 60 Merck 230−400 mesh. de ratios were calculated by ^{1}H NMR or ^{13}C NMR of the crude reaction mixtures. The ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ at room temperature unless otherwise indicated. Chemical shifts in ppm are referenced to Me_4Si.

General Procedure A. In a three-necked flask equipped with an alcohol thermometer, the morpholinyl chromium carbene (**1**, 1.0 mmol, 0.333 g) or the piperidinyl chromium carbene (**2**, 1.0 mmol, 0.331 g) was dissolved in dry THF (48.7 mL, 2.05×10^{-2} M solution). The solution was cooled to −78 °C under magnetic stirring. A hexane solution of *n*-buthyllithium (1.0 mmol) was added dropwise and allowed to react at −78 °C for 30 min.[16] Then a precooled solution of the appropriate nitroalkene (1.0 mmol) in THF (6 mL) was added during 20 min, and the mixture was allowed to react for a further 30 min or as otherwise indicated in Tables 1−5. Then a saturated ammonium chloride solution was added, and the reaction vessel was brought to room temperature. The THF was evaporated under vacuum, and the mixture was extracted with dichloromethane (3 × 20 mL), dried over Na_2SO_4, and filtered over a Celite pad. After removal of the solvent under reduced pressure, column chromatography gave the desired addition products. Usually light petroleum/dichloromethane mixtures of eluents and vacuum chromatography were used to isolate adducts from starting compounds, while light petroleum/ethyl acetate mixtures and flash chromatography served to separate diastereomers from each other.

General Procedure B. The procedure was similar to A, but the concentration of the reagents was 10-fold (or as otherwise indicated in Table 4). For the reaction involving the concentration of 0.20 M, only 5.0 mL of THF was added to dissolve the starting compound.

General Procedure C: Reaction with 12-Crown-4 Ether. The procedure was similar to A, except for the addition of 12-crown-4 30 min after the addition of BuLi. Then, after 30 min of equilibration, the nitroalkene was added and the reaction was carried out as in procedure A.

While yields and de's are reported in the corresponding tables, hereafter are reported the spectral data of addition products. Assignment of signals was made with the aid of NMR bidimensional experiments (COSY) or correlation with ^{1}H NMR of similar compounds.

***p*-NO$_2$ 6c** (major diastereoisomer): yellow-orange solid, mp 139−141 °C dec (diethyl ether/pentane). IR (Nujol): ν 2054 (CO *trans*), 1914 (CO *cis*), 1559 (NO_2), 1422 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (d, $^3J = 6.5$ Hz, 3H, CH_{3ax}), 1.29 (d, $J = 6.3$ Hz, 3H, CH_{3eq}), 3.40 (dd, $^2J = 13.6$ Hz, $^3J = 6.3$ Hz, 1 H, N−CHH_{ax}), 3.73 (m, 2 H, Cr═CCH$_2$), 3.82 (dd, $^2J = 13.2$ Hz, $^3J = 8.7$ Hz, 1 H, N-CH_{ax}H), 3.88 (dd, $^2J = 13.3$ Hz, $^3J = 3.5$ Hz, 1 H, N-CH_{eq}H), 4.00 (m, 1 H, Ph-C*H*), 4.20−4.20 (m, 2 H, CH_3C*H*-O), 4.50 (bd, $^2J = 13.0$ Hz, 1 H, N-CHH_{eq}), 4.73 (d, $J = 7.4$ Hz, 2 H, CH_2NO$_2$), 7.35 (m, 2 H, H arom), 8.25 (m, 2 H, H arom). ^{13}C NMR ($CDCl_3$): δ 16.6 (CH_{3ax}), 17.6 (CH_{3eq}), 41.5 (Ph-*C*H), 53.6 (*C*H$_2$C═Cr), 58.2 (N-CH$_2$), 66.9 (N-CH$_2$), 67.7 (CH_3*C*H-O), 77.9 (CH_2NO_2), 124.4, 128.5 (CH arom, 144.3 (Cq arom), 147.8 (O$_2$N-Cq arom), 217.2 (CO *cis*), 222.0 (CO *trans*), 278.7 (C═Cr). MS (FAB$^+$): *m/z* 527 (M$^+$) [2], 499 (M$^+$ − CO) [2], 443 (M$^+$ − 3CO) [1], 415 (M$^+$ − 4CO) [20], 397 (M$^+$ − 3CO − NO$_2$) [7], 387 (M$^+$ − 5CO) [4], 369 (M$^+$ − 4CO − NO$_2$) [24], 336 (M$^+$ − Cr(CO)$_5$ + 1) [23], 302 [100]. $C_{21}H_{21}N_3O_{10}$ Cr (527.40): calcd C 47.8, H 4.0, N 8.0; found C 48.0, H 4.4, N 8.4.

7c (minor diastereoisomer): yellow-orange solid mp 135−138 °C dec (diethyl ether/pentane). ^{1}H NMR ($CDCl_3$): δ 1.13 (d, $J = 6.6$ Hz, 3H, CH_{3ax}), 1.23 (d, $J = 6.6$ Hz, 3H, CH_{3eq}), 3.10−3.20 (dd, $^2J = 12.9$ Hz, $^3J = 3.5$ Hz, 1 H, Cr═CC*H*H, superimposed to dd, $^2J = 12.8$ Hz, $^3J = 8.6$ Hz, 1 H, N-CHH_{ax}), 3.44 (br dd, $^2J = 12.9$ Hz, $^3J = 3.8$ Hz, 1 H, N-CH_{eq}H), 3.65 (dd, $^2J = 13.0$ Hz, $^3J = 8.3$ Hz, 1H, N-CHH_{ax}), 3.85 (dd, $^2J = 12.8$ Hz, $^3J = 7.2$ Hz, 1H, Cr═CCH*H*), 3.90 (m, 2H, Ph-C*H* + CH_{3eq}C*H*-O), 4.23 (m, 1 H, CH_{3ax}C*H*-O), 4.56 (br d, $^2J = 12.5$ Hz, 1 H, N-CHH_{eq}), 4.85 (dd, A part of an ABX system, $^2J = 13.3$ Hz, $^3J = 5.2$ Hz, 1 H, C*H*HNO$_2$), 4.93 (dd, B part of an ABX system, $^2J = 13.3$ Hz, $^3J = 10.0$ Hz, 1 H, CH*H*NO$_2$), 7.40 (m, 2 H, H arom), 8.25 (m, 3 H, H arom). ^{13}C NMR ($CDCl_3$): δ 16.6 (CH_{3ax}), 17.3 (CH_{3eq}), 41.5 (Ph-*C*H), 53.6 (*C*H$_2$C═Cr), 57.9 (N−CH$_2$), 66.8 (CH_3CH−O), 66.9 (N−CH$_2$), 67.6 (CH_3*C*H−O), 77.9 (CH_2NO_2), 124.4, 128.4 (CH arom), 144.2 (Cq arom), 147.8 (O$_2$N−Cq arom), 217.2 (CO *cis*), 222.0 (CO *trans*), 275.4 (C═Cr).

***p*-CH$_3$ 6d** (major diastereoisomer): yellow thick oil. IR (Nujol): ν 2053 (CO *trans*), 1914 (CO *cis*), 1557, 1380 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.10 (d, $^3J = 6.5$ Hz, 3H, CH_{3ax}), 1.30 (d, $J = 6.4$ Hz, 3H, CH_{3eq}), 2.40 (s, 3 H, Ar−CH$_3$), 3.14 (dd, $^2J = 13.1$ Hz, $^3J = 6.2$ Hz, 1 H, N-CHH_{ax}), 3.40 (dd, $^2J = 13.1$ Hz, $^3J = 5.4$ Hz, 1 H, Cr═CC*H*H), 3.60 (dd, $^2J = 13.0$ Hz, $^3J = 9.7$ Hz, 1 H, Cr═CCH*H*), 3.80 (dd, $^2J = 13.1$ Hz, $^3J = 3.3$ Hz, 1 H, N-CH_{eq}H), 3.90 (m, 1 H, Ph-C*H*), 3.96 ($^2J = 13.2$ Hz, $^3J = 7.7$ Hz, 1H, N-CHH_{ax}), 4.10 (m, 1 H, CH_{3eq}C*H*-O), 4.24

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[14] Licandro, E.; Maiorana, S.; Baldoli, C.; Capella, L.; Perdicchia, D. *Tetrahedron: Asymmetry* **2000**, *11*, 975−980, and references therein.

[15] (*E*)-*p*-Cl-nitrostyrene was exposed under sunlight at room temperature for a week. After purification by column chromatography, the (*Z*)-nitroalkene **10b** was isolated as a yellow solid (mp 33−35 °C, 70% yield).

[16] The procedure A has been performed also at different temperatures (−97 and −108 °C) as reported by us.[3,14]

(m, 1 H, $CH_{3ax}CH$-O), 4.40 (dd, $^2J = 13.2$ Hz, $^3J = 2.9$ Hz, 1 H, N-CHH_{eq}), 4.70 (d, $J = 7.6$ Hz, 2 H, CH_2NO$_2$), 7.02 (m, 2 H, H arom), 7.10 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 17.4 (CH_{3ax}), 17.2 (CH_{3eq}), 21.0 (Ar-*C*H$_3$), 41.4 (Ar-*C*H), 54.1 (*C*H$_2$C═Cr), 57.7 (N-CH$_2$), 65.8 (CH$_3$*C*H-O), 66.1 (N-CH$_2$), 67.2 (CH$_3$*C*H-O), 78.8 (CH$_2$NO$_2$), 127.2, 129.9, (CH arom), 138.5, 141.6 (Cq arom), 217.5 (CO *cis*), 222.4 (CO *trans*), 278.3 (C═Cr). MS (FAB$^+$): *m/z* 496 (5) [M$^+$], 466 (10) [M$^+$ − NO], 440 (13) [M$^+$ − 2CO], 412 (15) [M$^+$ − 3CO], 384 (16) [M$^+$ − 4CO], 353 (10) [M$^+$ − 4CO − HNO], 339 (26) [M$^+$ − 4CO − NO$_2$ + 1], 305 (90) [M$^+$ − Cr(CO)$_5$], 259 (54) [M$^+$ − Cr(CO)$_5^-$ NO$_2$]. $C_{22}H_{24}N_2O_8$-Cr (496.43): calcd C 53.2, H 4.8, N 5.65; found C 53.2, H 5.4, N 6.0.

7d (minor diastereoisomer): yellow solid, mp = 94−96 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.06 (d, $J =$ 6.5 Hz, 3 H, CH_{3ax}), 1.20 (d, $J = 6.3$ Hz, 3 H, CH_{3eq}), 2.36 (s, 3 H, Ar-CH$_3$), 2.90 (dd, $^2J = 13.1$ Hz, $^3J = 3.6$ Hz, 1 H, N-CHH_{ax}), 3.17 (dd, $^2J = 12.6$ Hz, $^3J = 9.1$ Hz, 1 H, Cr═CC*H*H), 3.30 (dd, $^2J = 13.1$ Hz, $^3J = 4.5$ Hz, 1 H, N-CH_{eq}H), 3.62 (m, 1H, Ph-C*H*), 3.68 (dd, $^2J = 13.1$ Hz, $^3J = 8.0$ Hz, 1H, N-CHH_{ax}), 3.74 (dd, $^2J = 12.7$ Hz, $^3J = 5.4$ Hz, 1H, Cr═CCH*H*), 3.87 (m, 1 H, CH_{3eq}C*H*-O), 4.20 (m, 1 H, CH_{3ax}C*H*-O), 4.52 (dt, $^2J = 13.1$ Hz, $^3J = 1.5$ Hz, 1 H, N-CHH_{eq}), 4.82 (dd, A part of ABX system, $^2J = 12.7$ Hz, $^3J = 5.6$ Hz, 1H, C*H*HNO$_2$), 4.90 (dd, B part of ABX system, $^2J = 12.7$ Hz, $^3J = 5.6$ Hz, 1 H, CH*H*NO$_2$) 7.20 (m, 2 H, H arom), 7.40 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH_{3ax}), 17.3 (CH_{3eq}), 21.1 (Ar-*C*H$_3$), 42.1 (Ar-*C*H), 53.6 (*C*H$_2$C═Cr), 57.5 (N-CH$_2$), 66.9 (CH$_3$*C*H-O), 67.0 (N-CH$_2$), 67.3 (CH$_3$*C*H-O), 79.0 (CH$_2$NO$_2$), 127.5, 130.1 (CH arom), 139.0, 142.8 (Cq arom), 217.6 (CO *cis*), 222.2 (CO *trans*), 291.9 (C═Cr).

***p*-OCH$_3$ 7e** (major diastereoisomer): yellow solid, mp 84−85 °C dec (diethyl ether/pentane). IR (Nujol): ν 2052 (CO *trans*), 1908 (CO *cis*), 1556 (NO$_2$), 1379 (NO$_2$), 1253 (C-OMe) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.05 (d, $^3J = 6.6$ Hz, 3H, CH_{3ax}), 1.19 (d, $J = 6.3$ Hz, 3H, CH_{3eq}), 2.87 (dd, $^2J = 13.0$ Hz, $^3J =$ 3.4 Hz, 1 H, N-CHH_{ax}), 3.13 (dd, $^2J = 12.6$ Hz, $^3J = 9.2$ Hz, 1 H, Cr═CC*H*H), 3.30 (ddd, $^2J = 13.0$ Hz, $^3J = 4.15$ Hz, $^4J_{(through\ N)} = 1.2$ Hz, 1 H, N-CH_{eq}H), 3.60−3.70 (dd, $^2J = 12.6$ Hz, $^3J =$ 5.0 Hz, 1 H, Cr═CCH*H*, + dd, $^2J = 13.1$ Hz, $^3J = 8.1$ Hz, 1H, N-CHH_{ax}, superimposed to m, 1 H, CH_{3ax}C*H*-O), 3.78 (s, 3H, OMe), 3.80−3.90 (m, 1 H, Ph-C*H*), 4.18 (m, 1 H, CH_{3ax}C*H*-O), 4.50 (br dt, $^2J = 13.1$ Hz, $J = 1.2$ Hz, 1 H, N-CHH_{eq}), 4.78 (dd, A part of an ABX system, $^2J = 12.6$ Hz, $^3J = 5.8$ Hz, 1 H, C*H*HNO$_2$), 4.85 (dd, B part of an ABX system, $^2J = 12.6$ Hz, $^3J = 10.0$ Hz, 1 H, CH*H*NO$_2$), 6.80−6.90 (m, 2 H, H arom), 7.00−7.10 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH_{3ax}), 17.4 (CH_{3eq}), 41.8 (Ph-*C*H), 53.8 (*C*H$_2$C═Cr), 55.4 (CH$_3$O), 57.5 (N-CH$_2$), 66.8 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 67.4 (CH$_3$*C*H-O), 79.1 (CH$_2$NO$_2$), 114.8, 128.7 (CH arom), 128.8 (Cq arom), 159.6 (O-Cq arom), 217.6 (CO *cis*), 222.2 (CO *trans*), 273.9 (C═Cr). MS (FAB$^+$): *m/z* 512 (10) [M$^+$], 484 (8) [M$^+$ − CO], 428 (95) [M$^+$ − 3CO], 400 (58) [M$^+$ − 4CO], 372 (5) [M$^+$ − 5CO], 354 (38) [M$^+$ − 4CO − NO$_2$], 341(8) [M$^+$ − 5CO − CH$_3$O], 321 (27) [M$^+$ − Cr(CO)$_5$ + 1], 287 (100), 274 (18) [M$^+$ − Cr(CO)$_5$ − NO$_2$]. $C_{22}H_{24}N_2O_9Cr$ (512.43): calcd C 51.60, H 4.70, N 5.50; found C 52.10, H 4.75, N 5.40.

6e (minor diastereoisomer): yellow solid mp = 82−84 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.10 (d, $J = 6.5$ Hz, 3H, CH_{3ax}), 1.30 (d, $J = 6.5$ Hz, 3H, CH_{3eq}), 3.15 (dd, $^2J =$ 13.2 Hz, $^3J = 6.1$ Hz, 1 H, N-CHH_{ax}), 3.40 (dd, $^2J = 13.1$ Hz, $^3J = 5.4$ Hz, 1 H, Cr═CC*H*H), 3.60 (dd, $^2J = 13.1$ Hz, $^3J = 9.7$ Hz, 1 H, Cr═CCH*H*), 3.75 (dd, $^2J = 13.2$ Hz, $^3J = 3.3$ Hz, 1H, N-CH_{eq}H), 3.78 (s, 1H, OMe), 3.80−3.90 (m, 1H, Ph-C*H*), 3.90 (dd, $^2J = 13.2$ Hz, $^3J = 7.7$ Hz, 1H, N-CHH_{ax}), 4.10 (m, 1 H, CH_{3eq}C*H*-O), 4.20 (m, 1 H, CH_{3ax}C*H*-O), 4.37 (br dd, $^2J = 13.2$ Hz, $^3J = 3.1$ Hz, 1 H, N-CHH_{eq}), 4.70 (d, 2 H, $^2J = 7.6$ Hz, CH_2NO$_2$), 6.80−6.90 (m, 2 H, H arom), 7.00−7.10 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): $\delta = 17.1$ (CH_{3ax}), 17.3 (CH_{3eq}), 41.1 (Ph-*C*H), 54.2 (*C*H$_2$C═Cr), 55.3 (O−CH$_3$), 57.8 (N-CH$_2$), 66.1 (N-CH$_2$), 66.9 (CH$_3$*C*H-O), 67.2 (CH$_3$*C*H-O), 79.0 (CH$_2$NO$_2$), 114.7, 128.5 (CH arom), 128.9 (Cq arom), 159.6 (O-Cq arom), 217.6 (CO *cis*), 222.5(CO *trans*), 278.2 (C═Cr).

***p*-N(CH$_3$)$_2$ 7f** (major diastereoisomer): pale yellow solid, mp 181−183 °C dec (diethyl ether/pentane). IR (Nujol): ν 2052 (CO *trans*), 1970 (CO *cis*), 1556, 1380 (NO$_2$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.03 (d, $^3J = 6.5$ Hz, 3 H, CH_{3ax}), 1.19 (d, $J = 6.4$ Hz, 3 H, CH_{3eq}), 2.83 (dd, $^2J = 13.2$ Hz, $^3J = 3.4$ Hz, 1 H, N-CHH_{ax}), 2.92 (s, 6 H, N(CH$_3$)$_2$), 3.12 (dd, $^2J = 12.2$ Hz, $^3J =$ 9.3 Hz, 1 H, Cr═CC*H*H), 3.29 (ddd, $^2J = 13.2$ Hz, $^3J = 3.1$ Hz, $^3J = 1.5$ Hz, 1 H, N-CH_{eq}H), 3.60−3.70 (m, 1 H, Ph-C*H*, superimposed to dd, $^2J = 12.8$ Hz, $^3J = 7.8$ Hz, 1 H, N-CHH_{ax}), 3.72 (dd, $^2J = 12.2$ Hz, $^3J = 4.8$ Hz, 1 H, Cr═CCH*H*), 3.78 (m, 1 H, CH_{3ax}C*H*-O), 4.20 (m, 1 H, CH_{3eq}C*H*-O), 4.50 (br d, $^2J =$ 12.8 Hz, 1 H, N-CHH_{eq}), 4.72−4.87 (AB part of ABX system, A: $^2J = 12.4$ Hz, $^3J = 6.0$ Hz, 1 H, B: $^2J = 12.4$ Hz, $^3J = 9.9$ Hz, 1 H, CH_2NO$_2$), 6.60 (m, 2 H, H arom), 7.00 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH_{3ax}), 17.4 (CH_{3eq}), 40.3 (N(CH$_3$)$_2$), 41.7 (Ph-*C*H), 53.9 (*C*H$_2$C═Cr), 57.4 (N-CH$_2$), 66.9 (CH$_3$*C*H-O), 67.1 (N-CH$_2$), 67.4 (CH$_3$*C*H-O), 79.3 (CH$_2$NO$_2$), 112.7, 128.3 (CH arom), 123.5 (Cq arom), 150.5 (N-Cq arom), 217.7 (CO *cis*), 222.8 (CO *trans*), 273.4 (C═Cr). MS (FAB$^+$): *m/z* 525 (7) [M$^+$], 497 (18) [M$^+$ − CO], 469 (10) [M$^+$ − 2CO], 441 (100) [M$^+$ − 3CO], 413 (16) [M$^+$ − 4CO], 385 (14) [M$^+$ − 5CO], 367 (64) [M$^+$ − 4CO − NO$_2$], 354 (28) [M$^+$ − 5CO − HNO], 338 (23) [M$^+$ − 5CO − HNO$_2$]. 334 (32) [M$^+$ − Cr(CO)$_5$ + 1], 287 [M$^+$ − Cr(CO)$_5$ − NO$_2$]. $C_{23}H_{27}N_3O_8Cr$ (525.47): calcd C 52.6, H 5.2, N 8.0; found C 52.0, H 4.8, N 7.7.

6f (minor diastereoisomer): pale yellow solid, mp 169 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.08 (d, $J = 6.4$ Hz, 3 H, CH_{3ax}), 1.27 (d, $J = 6.4$ Hz, 3 H, CH_{3eq}), 2.91 (s, 6 H, N(CH$_3$)$_2$), 2.96 (dd, $^2J = 13.2$ Hz, $^3J = 3.6$ Hz, 1 H, N-CHH_{ax}), 3.38 (dd, $^2J = 12.9$ Hz, $^3J = 5.2$ Hz, 1 H, Cr═CC*H*H), 3.53 (dd, $^2J = 12.9$ Hz, $^3J = 9.8$ Hz, 1 H, Cr═CCH*H*), 3.72 (dd, $^2J = 13.2$ Hz, $^3J = 3.3$ Hz, 1H, N-CHH_{ax}), 3.82 (m, 1H, Ph-C*H*), 3.98 (dd, $^2J = 13.1$ Hz, $^3J = 7.3$ Hz, 1 H, N-CH_{eq}H), 4.05 (m, 1 H, CH_{3eq}C*H*-O),4.20 (m, 1 H, CH_{3ax}C*H*-O), 4.30 (dd, $^2J = 13.1$ Hz, $^3J = 3.0$ Hz, 1 H, N-CHH_{ax}), 4.72 (d, $J = 7.7$ Hz, 2 H, CH_2NO$_2$), 6.60 (m, 2 H, H arom), 6.90 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 17.2 (CH_{3ax}), 17.4 (CH_{3eq}), 40.3 (N(CH$_3$)$_2$), 41.1 (Ph-*C*H), 54.3 (*C*H$_2$C═Cr), 57.6 (N-CH$_2$), 65.8 (N-CH$_2$), 66.6 (CH$_3$*C*H−O), 67.0 (CH$_3$*C*H-O), 79.1 (CH$_2$NO$_2$), 112.6, 128.1, (CH arom), 123.5 (Cq arom), 150.5 (N−Cq arom), 217.6 (CO *cis*), 214.0 (CO *trans*), 273.4 (C═Cr).

***o*-NO$_2$ 6g** (major diastereoisomer): bright yellow solid, mp 127−128 °C dec (diethyl ether/pentane). IR (Nujol): ν 2053 (CO *trans*), 1908 (CO *cis*), 1557 (NO$_2$ str. as), 1377 (NO$_2$ str. s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.24 (d, $^3J = 6.5$ Hz, 3H, CH_{3ax}), 1.28 (d, $J = 6.3$ Hz, 3H, CH_{3eq}), 3.50 (dd, $^2J = 13.8$ Hz, $^3J =$ 6.9 Hz, 1 H, N-CHH_{ax}), 3.80 (dd, $^2J = 13.3$ Hz, $^3J = 9.2$ Hz, 1 H, superimposed to dd, $^2J = 13.6$ Hz, $^3J = 9.1$ Hz, 1 H, N-CH_{eq}H + N-CHH_{ax}), 4.00 (apparent d, 2 H, Cr═CCH$_2$), 4.26 (m, 2 H, Ph-C*H* + CH_{3ax}C*H*-O), 4.52 (m, 2 H, CH_{3eq}C*H*-O + N-CHH_{eq}), 4.70 (dd A part of ABX, $^2J = 13.8$ Hz, $^3J = 7.1$ Hz, 1 H, CH*H*NO$_2$), 4.80 (dd B part of ABX, $^2J = 13.8$ Hz, $^3J = 7.1$ Hz, 1 H, C*H*HNO$_2$), 7.47 (m, 1 H, H arom), 7.60 (d, $^3J = 7.7$ Hz, 1 H, H arom), 7.70 (t, $J = 7.6$ Hz, 1 H, H arom), 7.83 (d, $^3J = 8.1$ Hz, 1 H, H arom *ortho*). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH_{3ax}), 17.8 (CH_{3eq}), 34.8 (Ar-*C*H), 54.3 (*C*H$_2$C═Cr), 58.1 (N-CH$_2$), 66.5 (CH$_3$*C*H-O), 66.9 (N-CH$_2$), 68.0 (CH$_3$*C*H-O), 77.7 (CH$_2$NO$_2$), 125.2, 128.9, 129.3 (CH arom), 132.0 (Cq arom), 134.0 (CH arom), 138.5 (Cq arom), 217.2 (CO *cis*), 222.2 (CO *trans*), 277.3 (C═Cr). MS (FAB$^+$): *m/z* 527 (M$^+$) [20], 499 (M$^+$ − CO) [10], 471 (M$^+$ − 2CO) [1], 415 (M$^+$ − 4CO) [40], 387 (M$^+$ − 5CO) [10], 336 (M$^+$ − Cr(CO)$_5$ + 1) [30], 307 [70], 289 (M$^+$ − Cr(CO)$_5$ −HNO$_2$) [50], 257 [100], 242 (M$^+$ − Cr(CO)$_5$ − HNO$_2$ − NO$_2$) [100]. $C_{21}H_{21}N_3O_{10}Cr$ (527.40): calcd C 47.8, H 4.0, N 8.0; found C 48.1, H 4.3, N 8.2.

7g (minor diastereoisomer): bright yellow solid, mp 127−129 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.28 (d, $J = 6.5$ Hz, 6 H, CH_{3ax} + CH_{3eq}), 3.43 (dd, $^2J = 14.0$ Hz, $^3J = 6.3$ Hz, 1 H, N−CHH_{ax}), 3.86 (dd, $^2J = 13.0$ Hz, $^3J = 5.2$ Hz, 1 H, Cr=CC*H*H), 3.96 (dd, ^2J = 12.9 Hz, ^3J = 7.1 Hz, 1 H, N-CH*H*$_{ax}$), 4.06 (m, 1H, Cr=CCH*H*, superimposed to dd, ^2J = 14.0 Hz, ^3J = 11.3 Hz, 1H, N-C*H*$_{eq}$H), 4.20 (m, 1H, CH$_{3ax}$C*H*-O), 4.36 (m, 2 H, Ar-C*H* + CH$_{3eq}$C*H*-O), 4.53 (dd, ^2J = 12.9 Hz, ^3J = 3.1 Hz, 1 H, N-CH*H*$_{eq}$), 4.70 (dd, A part of ABX system, ^2J = 13.7 Hz, ^3J = 4.4 Hz, 1 H, C*H*HNO$_2$), 5.02 (dd, B part of ABX system, ^2J = 13.7 Hz, ^3J = 10.6 Hz, 1 H, CH*H*NO$_2$), 7.50 (m, 1 H, H arom), 7.75 (m, 2 H, H arom), 7.9 (d, ^3J = 8.1 Hz, 1 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.7 (CH$_{3ax}$), 17.1(CH$_{3eq}$), 36.5 (Ph-*C*H), 54.4 (*C*H$_2$C=Cr), 58.5 (N-CH$_2$), 66.9 (N-CH$_2$), 67.2 (CH$_3$*C*H-O), 67.4 (CH$_3$*C*H-O), 77.3 (CH$_2$NO$_2$), 125.1, 127.9, 129.2 (CH arom), 131.8 (Cq arom), 134.1 (CH arom), 138.5 (Cq arom), 217.1 (CO *cis*), 221.9 (CO *trans*), 276.6 (C=Cr).

***m*-NO$_2$ 6h** (major diastereoisomer): yellow solid, mp 140 °C dec (diethyl ether/pentane). IR (Nujol): ν 2053 (CO *trans*), 1903 (CO *cis*), 1557 (NO$_2$ str. as), 1352 (NO$_2$ str. s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.22 (d, ^3J = 6.6 Hz, 3H, CH$_{3ax}$), 1.29 (d, J = 6.3 Hz, 3H, CH$_{3eq}$), 3.37 (dd, ^2J = 13.6 Hz, ^3J = 5.9 Hz, 1 H, N-CH*H*$_{ax}$), 3.70−3.85 (m, 3 H, Cr=CCH$_2$ + N-C*H*$_{eq}$H), 3.88−4.05 (m, 1 H, Ph-C*H* superimposed to dd, ^2J = 12.6 Hz, ^3J = 3.5 Hz, N−C*H*$_{eq}$H), 4.20−4.32 (m, 2 H, CH$_{3eq}$C*H*-O + CH$_{3ax}$C*H*-O), 4.56 (br dt, ^2J = 13.1 Hz, ^3J = 1.7 Hz, 1 H, N-CH*H*$_{eq}$), 4.76 (d, J = 7.4 Hz, 2 H, C*H*$_2$NO$_2$), 7.50−7.60 (m, 2 H, H arom), 8.00 (br s, 1 H, H arom.), 8.20 (br d, 1 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH$_{3ax}$), 17.7 (CH$_{3eq}$), 41.3 (Ph-*C*H), 53.8 (*C*H$_2$C=Cr), 58.4 (N-CH$_2$), 66.8 (CH$_3$*C*H-O), 67.0 (N-CH$_2$), 67.9 (CH$_3$*C*H-O), 77.9 (CH$_2$NO$_2$), 122.4, 123.5, 130.5,133.6 (CH arom), 139.0 (Cq arom), 148.5 (Cq-NO$_2$ arom), 217.2 (CO *cis*), 222.1 (CO *trans*), 278.9 (C=Cr). C$_{21}$H$_{21}$N$_3$O$_{10}$Cr (527.40): calcd C 47.80, H 4.00, N 8.00; found C 47.32, H 4.24, N 7.95.

7h (minor diastereoisomer): mp 138−139 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.13 (d, J = 6.6 Hz, 3H, CH$_{3ax}$), 1.22 (d, J = 6.4 Hz, 3H, CH$_{3eq}$), 3.18 (dd, 1 H, ^2J = 12.9 Hz, ^3J = 3.8 Hz, superimposed to dd, ^2J = 13.1 Hz, ^3J = 7.5 Hz, 1 H, N-CH*H*$_{ax}$ + Cr=CC*H*H), 3.45 (br dd, ^2J = 12.9 Hz, ^3J = 4.2 Hz, 1 H, Cr=CCH*H*), 3.69 (dd, ^2J = 13.1 Hz, ^3J = 8.2 Hz, 1H, N-CH*H*$_{ax}$), 3.80−3.90 (dd, ^2J = 13.1 Hz, ^3J = 7.2 Hz, 1H, N-C*H*$_{eq}$H), 3.88 (m, 1 H, Ph-C*H*), 3.97 (m, 1H, CH$_{3eq}$C*H*-O), 4.20−4.30 (m, 1 H, CH$_{3eq}$C*H*-O),4.58 (br d, ^2J = 13.3 Hz, 1 H, N-CH*H*$_{eq}$), 4.86 (dd, A part of ABX system, ^2J = 13.2 Hz, ^3J = 5.1 Hz, 1 H, C*H*HNO$_2$), 4.94 (dd, B part of ABX system, ^2J = 13.2 Hz, ^3J = 10.1 Hz, 1 H, CH*H*NO$_2$), 7.50−7.70 (m, 2 H, H arom), 8.10 (bs, 1 H, H arom), 8.25 (br d, 1 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH$_{3ax}$), 17.3 (CH$_{3eq}$), 42.3 (Ph-*C*H), 53.2 (*C*H$_2$C=Cr), 57.9 (N-CH$_2$), 66.8 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 67.5 (CH$_3$*C*H-O), 78.0 (CH$_2$NO$_2$), 122.4, 123.5, 130.6, 133.5 (CH arom), 139.9 (Cq arom), 148.5 (Cq-NO$_2$ arom), 217.3 (CO *cis*), 221.9 (CO *trans*), 275.5 (C=Cr).

Ph(CO)$_3$Cr 6i (major diastereoisomer): yellow solid, mp 116−118 °C dec (diethyl ether/pentane). IR (Nujol): ν 2054 (CO trans), 1971−1900 (Cr(CO)$_3$, 1898 (CO cis), 1557 and 1458 (NO$_2$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.24 (d, ^3J = 6.3 Hz, 3H, CH$_{3ax}$), 1.31 (d, J = 6.2 Hz, 3H, CH$_{3eq}$), 3.30 (dd, ^2J = 13.0 Hz, ^3J = 3.7 Hz, 1 H, Cr=CC*H*H), 3.40 (m, 1 H, Ph-C*H*), 3.73 (dd, ^2J = 12.9 Hz, ^3J = 10.4 Hz, 1 H, N-CH*H*$_{ax}$), 3.77 (dd, ^2J = 13.0 Hz, ^3J = 10.0 Hz, 1 H, Cr=CCH*H*), 3.93 (dd, ^2J = 12.7 Hz, ^3J = 3.8 Hz, 1 H, N-CH*H*$_{ax}$), 4.10 (dt, 1 H, ^2J = 12.7 Hz, ^3J = 1.2 Hz, 1H, N-C*H*$_{eq}$H), 4.25−4.35 (m, 2 H, CH$_{3eq}$C*H*-O + CH$_{3ax}$C*H*-O), 4.60 (dd, ^2J = 13.8 Hz, ^3J = 9.7 Hz, 1 H, C*H*HNO$_2$), 4.70 (br d, ^2J = 12.9 Hz, ^3J = 1.2 Hz,1 H, N-CH*H*$_{eq}$), 4.79 (dd, ^2J = 13.8 Hz, ^3J = 4.1 Hz, 1 H, CH*H*NO$_2$), 4.89 (d, ^3J = 6.5 Hz 1 H, H*o* arom complex η^6), 5.15 (d, ^3J = 6.2 Hz 1 H, H*o* arom complex η^6), 5.32 (dd, ^3J = 11.0 Hz, ^3J = 5.4 Hz, 2 H, H*m* arom complex η^6), 5.41 (t, ^3J = 6.3 Hz, 1H, H*p* arom complex η^6). ^{13}C NMR (CDCl$_3$): δ 16.1 (CH$_{3ax}$), 18.0 (CH$_{3eq}$), 39.5 (Ph-*C*H), 55.0 (*C*H$_2$C=Cr), 58.3 (N-CH$_2$), 66.4 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 68.4 (CH$_3$*C*H-O), 78.2 (CH$_2$NO$_2$), 91.4, 91.5, 93.0, 93.4 (CH arom complex η^6), 107.3 (Cq arom complex η^6), 217.0 (CO *cis*), 222.1 (CO *trans*), 231.6 (CO complex η^6), 279.4 (C=Cr). MS (FAB$^+$): *m/z* 506 (5) [M$^+$ − 4CO], 394 (70) [M$^+$ − 8CO], 290 (20) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$], 259 (65) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$ − HNO], 257 (100), 243 (20) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$ − HNO$_2$]. C$_{24}$H$_{22}$N$_2$O$_{11}$Cr$_2$ (618.43): calcd C 46.6, H 3.6, N 4.5; found C 46.2, H 3.2, N 4.0.

7i (minor diastereoisomer): mp 73−74 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.27 (d, ^3J = 6.3 Hz, 3H, CH$_{3ax}$), 1.30 (d, J = 6.2 Hz, 3H, CH$_{3eq}$), 3.20−3.30 (m, 2 H, Cr=CC*H*H + Ph-C*H*), 3.82 (dd, ^2J = 12.9 Hz, ^3J = 8.2 Hz, 1 H, N-CH*H*$_{ax}$), 3.85−4.20 (m, 3H, Cr=CCH*H*, N−CH*H*$_{ax}$, N-C*H*$_{eq}$H), 4.25 (m, 1 H, CH$_{3eq}$C*H*-O), 4.32 (m, 1 H, CH$_{3ax}$C*H*-O), 4.60 (br d, ^2J = 12.9 Hz, 1 H, N-CH*H*$_{eq}$), 4.68 (dd, A part of ABX system, ^2J = 13.0 Hz, ^3J = 8.7 Hz, 1 H, CH*H*NO$_2$), 4.72 (dd, B part of ABX system, ^2J = 13.0 Hz, ^3J = 5.0 Hz, 1 H, C*H*HNO$_2$), 5.16 (t, ^3J = 6.3 Hz 1 H, H*m* arom), 5.30 (m, 2 H, H*o* + *Hm arom* complex η^6), 5.47 (d, ^3J = 6.7 Hz, 1 H, H*o* arom complex η^6), 5.53 (t, ^3J = 6.3 Hz, 1H, H*p* arom complex η^6). ^{13}C NMR (CDCl$_3$): δ 16.2 (CH$_{3ax}$), 17.4 (CH$_{3eq}$), 40.7 (Ph-*C*H), 53.4 (*C*H$_2$C=Cr), 58.7 (N-CH$_2$), 66.8 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 67.8 (CH$_3$*C*H-O), 79.7 (CH$_2$NO$_2$), 89.3, 90.0, 92.2, 95.3, 95.5 (CH arom complex η^6), 108.0 (Cq arom complex η^6), 217.0 (CO *cis*), 222.1 (CO *trans*), 231.7 (CO complex η^6), 276.7 (C=Cr).

***p*-Cl−Ph(CO)$_3$Cr 6j** (major diastereoisomer): yellow solid, mp 118−120 °C dec (diethyl ether/pentane). IR (Nujol): ν 2054 (CO trans), 1978−1900 (Cr(CO)$_3$), 1903 (CO *cis*), 1557 and 1377 (NO$_2$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.27 (d, ^3J = 6.5 Hz, 3H, CH$_{3ax}$), 1.34 (d, J = 6.3 Hz, 3H, CH$_{3eq}$), 3.37 (m, 2 H, Cr=CC*H*H + Ph-C*H*), 3.70 (dd, ^2J = 16.0 Hz, ^3J = 12.0 Hz, 1 H, Cr=CCH*H*), 3.78 (dd, ^2J = 13.0 Hz, ^3J = 9.2 Hz, 1 H, N-CH*H*$_{ax}$), 3.93 (dd, ^2J = 12.7 Hz, ^3J = 3.7 Hz, 1 H, N-CH*H*$_{ax}$), 4.05 (ddd, ^2J = 12.7 Hz, ^3J = 3.6 Hz, ^3J = 1.9 Hz, 1H, N-C*H*$_{eq}$H), 4.32 (m, 2 H, CH$_{3eq}$C*H*-O + CH$_{3ax}$C*H*-O), 4.60 (m, 2 H, CH$_2$NO$_2$), 4.70 dt, ^2J = 13.0 Hz, ^3J = 1.9 Hz, 1 H, N-CH*H*$_{eq}$), 5.20 (dd, ^3J = 7.1 Hz, 1 H, H*o* arom), 5.40 (dd, ^3J = 7.1 Hz, 1 H, H*o* arom), 5.45 (m, 2 H, H*m* arom). ^{13}C NMR (CDCl$_3$): δ 16.3 (CH$_{3ax}$), 17.9 (CH$_{3eq}$), 39.1 (Ph-*C*H), 54.7 (*C*H$_2$C=Cr), 58.2 (N-CH$_2$), 66.5 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 68.2 (CH$_3$*C*H-O), 78.3 (CH$_2$NO$_2$), 89.7, 89.9, 91.9, 93.4 (CH arom complex η^6), 103.3, (Cq arom complex η^6), 113.4 (Cl−Cq arom complex η^6), 217.1 (CO *cis*), 221.9 (CO *trans*), 230.4 (CO complex η^6), 279.1 (C=Cr). MS (FAB$^+$): *m/z* 652 (10) [M$^+$], 624 (3) [M$^+$ − CO], 540 (8) [M$^+$ − 3CO], 460 (15) [M$^+$ − Cr(CO)$_5$], 428 (100) [M$^+$ − 8CO], 324 (10) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$], 293 (98) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$ − HNO], 291 (100), 277 (20) [M$^+$ − Cr(CO)$_5$ − Cr(CO)$_3$ − HNO$_2$]. C$_{24}$H$_{21}$ClN$_2$O$_{11}$Cr$_2$ (652.88): calcd C 44.15, H 3.2, N 4.3; found C 44.4, H 3.6, N 4.5.

7j (minor diastereoisomer): mp 100−103 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 1.26 (d, ^3J = 6.4 Hz, 3H, CH$_{3ax}$), 1.29 (d, J = 6.6 Hz, 3H, CH$_{3eq}$), 3.10 (m, 2 H, Cr=CCH$_2$), 3.65 (m, 1 H, Ph-C*H*), 3.75−4.20 (m, 3 H, N-CH*H*$_{ax}$ + N-CH*H*$_{ax}$ + N-C*H*$_{eq}$H), 4.22 (m, 1 H, CH$_{3ax}$C*H*-O), 4.37 (m, 1 H, CH$_{3eq}$C*H*-O), 4.60 (br d, ^2J = 13.0 Hz, 1H, N-C*H*$_{eq}$H), 4.70 (m, 2 H, CH$_2$NO$_2$), 5.30−5.45 (m + dd, ^3J = 6.8 Hz, 3 H, arom complex η^6), 5.56 (dd, 1 H, ^3J = 6.8 Hz, J = 1.7 Hz, H*o arom* complex η^6). ^{13}C NMR (CDCl$_3$): δ 16.2 (CH$_{3ax}$), 17.3 (CH$_{3eq}$), 40.2 (Ph-*C*H), 53.7 (*C*H$_2$C=Cr), 58.7 (N-CH$_2$), 66.8 (CH$_3$*C*H-O), 67.2 (N-CH$_2$), 67.8 (CH$_3$*C*H-O), 79.6 (CH$_2$NO$_2$), 88.6, 89.1, 91.8, 95.5 (CH arom complex η^6), 104.1, (Cq arom complex η^6), 111.5 (Cl−Cq arom complex η^6), 217.0 (CO *cis*), 221.8 (CO *trans*), 230.6 (CO complex η^6), 276.5 (C=Cr).

Py 6m (major diastereomer): brown-red solid, mp 120 °C dec (pentane). IR (Nujol): ν 2052 (CO *trans*), 1908 (CO *cis*), 1555 (NO$_2$), 1378 (NO$_2$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.19 (d, ^3J = 6.4 Hz, 3H, CH$_{3ax}$), 1.29 (d, J = 6.3 Hz, 3H, CH$_{3eq}$), 3.37 (dd, ^2J = 13.6 Hz, ^3J = 5.9 Hz, 1 H, N-CH*H*$_{ax}$), 3.55−3.70 (m, 2 H, Cr=CCH$_2$), 3.78−3.90 (m, 2H, N-C*H*$_{ax}$H + N-C*H*$_{eq}$H), 3.95 (m, 1 H, Py-C*H*), 4.16−4.30 (m, 2 H, CH$_3$C*H*-O), 4.53 (br.d, ^2J = 12.1 Hz, 1 H, N-CH*H*$_{eq}$), 4.73 (d, J = 7.0 Hz, 2 H, C*H*$_2$NO$_2$), 7.08 (m, 2 H, H Py), 8.60 (m, 2 H, Py). ^{13}C NMR (CDCl$_3$): δ 17.1 (CH$_{3ax}$), 18.0 (CH$_{3eq}$), 41.5 (Py-*C*H), 53.7 (*C*H$_2$C=Cr), 58.6 (N-CH$_2$), 67.2 (N-CH$_2$), 67.3 (CH$_3$*C*H-O), 67.9 (CH$_3$*C*H-O), 78.0

(CH_2NO_2), 122.9 (CH Py), 146.4 (Cq Py), 151.2 (N-CH Py), 217.6 (CO *cis*), 222.6 (CO *trans*), 278.8 (C=Cr). MS (FAB^+): *m*/*z* 484 ($M^+ + 1$) [10], 455 ($M^+ - CO$) [10], 427 ($M^+ - 3CO$) [3], 371 ($M^+ - 4CO$) [15], 344 ($M^+ - 5CO + 1$) [6] 325 ($M^+ - 4CO - NO_2$) [12], 292 ($M^+ - Cr(CO)_5 + 1$) [18], 245 ($M^+ - Cr(CO)_5 - NO_2$) [15], 258 [75]. $C_{20}H_{21}N_3O_8Cr$ (483.40): calcd C 49.7, H 4.4, N 8.7; found C 50.2, H 4.8, N 8.4.

7m (minor diastereoisomer): (from mixture of diastereomers) ^1H NMR ($CDCl_3$): δ 1.13 (d, $J = 6.6$ Hz, 3H, CH_{3ax}), 1.23 (d, $J = 6.6$ Hz, 3H, CH_{3eq}), 3.25 (dd, ^2J =12.9 Hz, $^3J = 3.5$ Hz, 1 H, Cr=CC*H*H, superimposed to dd, ^2J =12.8 Hz, $^3J = 8.6$ Hz, 1 H, N-CHH_{ax}), 3.50 (br dd, $^2J = 12.9$ Hz, $^3J = 3.8$ Hz, 1 H, N-CH_{eq}H), 3.62 (dd, $^2J = 13.0$ Hz, $^3J = 8.3$ Hz, 1H, N-CHH_{ax}), 3.80−3.90 (m, 1H, Cr=CCH*H*), 3.95−4.05 (m, 2H, Py-C*H* + CH_{3eq}C*H*-O), 4.20−4.30 (m, 1 H, CH_{3ax}C*H*-O), 4.65 (br d, $^2J =$ 12.5 Hz, 1 H, N-CHH_{eq}), 4.80−4.95 (m, AB part of an ABX system, 2 H, CH_2NO_2), 7.20 (m, 2 H, H Py), 8.60 (m, 2 H, H Py). ^{13}C NMR ($CDCl_3$): δ 16.8 (CH_{3ax}), 18.2 (CH_{3eq}), 41.1 (Py-*C*H), 53.8 (*C*H_2C=Cr), 58.8 (N-CH_2), 67.4 (CH_3*C*H-O), 67.6 (N-CH_2), 68.3 (CH_3*C*H-O), 78.0 (CH_2NO_2), 124.0 (CH Py), 148.5 (Cq Py), 156.3 (N-CH Py), 217.5 (CO *cis*), 222.0 (CO *trans*), 275.2 (C=Cr).

Synthesis of Complex 2. In a three-necked flask equipped with an alcohol thermometer, the pentacarbonyl[methoxy-(methyl)carbene]chromium complex (22 mmol, 5.5 g) was dissolved in dried THF (40 mL). The solution was cooled to −78 °C under magnetic stirring, then *trans*-3,5-dimethylpiperidine (27 mmol, 3.04 g) was added, and the mixture was allowed to react over a period of 7 h and then at −20 °C overnight. The THF was evaporated under vacuum. The residue was dissolved in dichloromethane and filtered over a Celite pad. After removal of the solvent under reduced pressure, column chromatography (light petroleum/dichloromethane, 9:1 to 1:1, then dichloromethane) afforded complex **2** as a pale yellow solid (16.7 mmol, 5.35 g) (75.9%). Mp: 53−54 °C (dichloromethane/*n*-pentane). IR (Nujol): ν 2055 (CO *trans*), 1958, 1917 (CO *cis*) cm $^{-1}$. ^1H NMR ($CDCl_3$): δ 0.95 (d, $^3J =$ 7.05 Hz, 3H, CH_{3ax}), 0.99 (d, $^3J = 6.66$ Hz, 3H, CH_{3eq}), 1.55 (ddd, $^2J = 13.29$ Hz, $^3J = 10.77$ Hz, $^3J = 4.85$ Hz, 1H, CH_3-CHCH*H*CHCH$_3$), 1.62 (dt, $^2J = 13.38$ Hz, $^3J = 3.95$ Hz, $^3J =$ 3.95 Hz, 1H, CH_3CHC*H*HCHCH$_3$), 2.14 (m, 2H, CH_3C*H*CH$_2$-C*H*CH$_3$), 2.68 (s, 3H, Cr=CCH_3), 3.35 (dd, $^2J = 12.70$ Hz, $^3J = 3.14$ Hz, 1H, NC*H*H), 3.36 (dd, $^2J = 14.2\ 0$ Hz, $^3J = 11.10$ Hz, 1H, NC*H*H), 4.08 (ddd, $^2J = 12.90$ Hz, $^3J = 3.75$ Hz, $^4J =$ 1.89 Hz, 1H, NCH*H*), 4.78 (ddd, $^2J = 14.40$ Hz, $^3J = 3.75$ Hz, $^4J = 1.85$ Hz, 1H, NCH*H*). ^{13}C NMR ($CDCl_3$): δ 17.10 (*C*H_{3ax}), 18.30 (*C*H_{3eq}), 28.76 (CH_3*C*H), 29.80 (CH_3*C*H), 39.26 (*C*H_3C=Cr + CH_3CH*C*H_2CHCH$_3$), 56.03 (CH_2N (*E*)), 68.87 (CH_2N (*Z*)), 217.91 (CO_{cis}), 269.95 (CO_{trans}). MS (EI): *m*/*z* 331 (5) (M^+), 303 (5) ($M^+ - 1CO$), 275 (5) ($M^+ - 2CO$), 247 (5) ($M^+ - 3CO$), 219 (10) ($M^+ - 4CO$), 191 (100) ($M^+ - 5CO$). $C_{14}H_{17}NO_5Cr$ (331.29): calcd C 50.75, H 5.17, N 4.23; found C 50.82, H 5.20, N 4.33.

Ph 8a (major diastereoisomer): pale yellow solid, mp 103−105 °C dec (diethyl ether/pentane). IR (Nujol): ν 2052 (CO *trans*), 1904 (CO *cis*), 1557, 1378 (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.90 (d, $^3J = 7.0$ Hz, 3H, CH_{3ax}), 1.00 (d, $J = 6.7$ Hz, 3H, CH_{3eq}), 1.60 (m, 1 H, CHH_{ax}), 1.90 (m, 1 H, CHH_{eq}), 2.30 (m, 2 H, C*H*-(CH_3)), 3.30 (dd, $^2J = 13.5$ Hz, $^3J = 6.0$ Hz, 1 H, Cr=CC*H*H), 3.55 (dd, $^2J =$ Hz, $^3J =$ Hz, 1 H, Cr=CCH*H*), 3.70 (dd, $^2J =$ Hz, $^3J =$ Hz, 1 H, N-CH_{eq}H), 3.95 (m, 1 H, Ph-C*H*), 4.45 (dd, $^2J = 13.0$ Hz, $^3J = 3.5$ Hz, 1 H, N-CHH_{eq}), 4.68 (m, 2 H, CH_2NO$_2$), 7.10−7.20 (m, 2 H, H arom), 7.20−7.40 (m, 3 H, H arom). ^{13}C NMR ($CDCl_3$): δ 17.1 (CH_{3ax}), 17.8 (CH_{3eq}), 28.1 (CH_3*C*H), 29.8 (CH_3*C*H), 39.2 (C-CH_2-C), (Ph-*C*H), 54.3 (*C*H_2C=Cr), 58.8 (N-CH_2), 69.0 (N-CH_2), 78.7 (CH_2NO_2), 127.4, 128.3, 129.2 (CH arom), 137.2 (Cq arom), 217.6 (CO *cis*), 222.9 (CO *trans*), 275.4 (C=Cr). MS (FAB^+): *m*/*z* 481 (7) [M^+], 453 (6) [$M^+ - CO$], 397 (20) [$M^+ - 3CO$], 369 (20) [$M^+ - 4CO$], 341 (14) [$M^+ - 5CO$], 323 (20) [$M^+ - 4CO - NO_2$], 310 (10) [$M^+ - 5CO - HNO$], 294 (5) [$M^+ - 5CO - HNO_2$], 290 (21) [$M^+ - Cr(CO)_5 + 1$], 256 (100), 242 (18) [$M^+ - Cr(CO)_5 - NO_2$]. $C_{22}H_{24}N_2O_7Cr$ (480.44): calcd C 55.0, H 5.0, N 5.8; found C 55.5, H 5.4, N 6.1.

9a (minor diastereoisomer): yellow solid, mp 87−89 °C dec (diethyl ether/pentane). ^1H NMR ($CDCl_3$): δ 0.84 (d, $^3J = 6.9$ Hz, 3H, CH_{3ax}), 0.94 (d, $J = 6.7$ Hz, 3H, CH_{3eq}), 1.43 (ddd, $^2J = 13.5$ Hz, $^3J = 10.8$ Hz, $^3J = 4.7$, 1 H, CHH_{ax}), 1.60 (dt, $^2J =$ 13.5 Hz, $^3J = 4.0$, 1 H, CHH_{eq}), 1.87 (m, 2 H, C*H*-CH_{3ax}), 2.19 (m, 2 H, C*H*-CH_{3eq}), 2.58 (dd, $^2J = 13.0$ Hz, $^3J = 3.1$ Hz, 1 H, N-CH_{ax}H), 3.17 (dd, $^2J = 12.8$ Hz, $^3J = 8.6$ Hz, 1 H, Cr=CC*H*H), 3.30 (dd, $^2J = 12.8$ Hz, $^3J = 10.3$ Hz, 1 H, N−CH_{ax}H), 3.44 (dd, $^2J = 13.0$ Hz, $^3J = 1.5$ Hz, 1 H, N-CHH_{eq}), 3.71 (dd, $^2J = 12.8$ Hz, $^3J = 6.1$ Hz, 1 H, Cr=CC*H*H), 3.85 (m, 1 H, Ph-C*H*), 4.51 (br d, $^2J = 12.8$ Hz, 1H, N-CHH_{eq}), 4.88 (dd, A part of ABX system, $^2J = 12.8$ Hz, $^3J = 4.9$ Hz, 1 H, CH*H*NO$_2$), 4.93 (dd, B part of ABX system, $^2J = 12.8$ Hz, $^3J = 10.8$ Hz, 1 H, C*H*HNO$_2$), 7.15 (m, 2 H, H arom), 7.25−7.40 (m, 3 H, H arom). ^{13}C NMR ($CDCl_3$): δ 16.9 (CH_{3ax}), 17.8 (CH_{3eq}), 28.3 (CH_3*C*H), 29.2 (CH_3*C*H), 38.6 (C-CH_2-C), 42.5 (Ph-*C*H), 53.9 (*C*H_2C=Cr), 58.2 (N-CH_2), 69.6 (N-CH_2), 78.6 (CH_2NO_2), 127.5, 128.4, 129.3 (CH arom), 137.6 (Cq arom), 217.8 (CO *cis*), 222.6 (CO *trans*), 271.6 (C=Cr).

***p*-Cl−Ph 8b** (major diastereoisomer): yellow solid, mp 51−54 °C dec (diethyl ether/pentane). IR (Nujol): ν 2051 (CO *trans*), 1908 (CO *cis*), 1556, 1378 (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.95 (d, $^3J = 7.0$ Hz, 3H, CH_{3ax}), 1.00 (d, $J = 6.6$ Hz, 3H, CH_{3eq}), 1.60 (m, 2 H, C-CH_2-C), 2.15−2.35 (m, 2 H, C*H*-(CH_3)), 3.30 (dd, $^2J = 13.4$ Hz, $^3J = 6.7$ Hz, 1 H, Cr=CC*H*H), 3.52 (dd, $^2J = 14.3$ Hz, $^3J = 9.8$ Hz, 1 H, NCHH_{ax}), 3.58 (dd, $^2J = 12.5$ Hz, $^3J = 3.3$ Hz, 1 H, Cr=CCH*H*), 3.70 (dd, $^2J = 13.4$ Hz, $^3J = 9.0$ Hz, 1 H, N-CH_{ax}H), 3.82 (dd, $^2J =$ 13.5 Hz, $^3J = 4.0$ Hz, 1 H, N-CHH_{eq}), 3.90 (m, 1 H, Ph-C*H*), 4.50 (br d, $^2J = 13.4$ Hz, 1H, N-CHH_{eq}), 4.63 (m, 2H, CH_2-NO_2), 7.10 (m, 2 H, H arom), 7.42 (m, 2 H, H arom). ^{13}C NMR ($CDCl_3$): δ 17.1 (CH_{3ax}), 17.8 (CH_{3eq}), 28.32 (CH_3*C*H), 30.0 (CH_3*C*H), 38.7 (C-CH_2-C), 41.3 (Ph-*C*H), 54.1 (*C*H_2C=Cr), 59.0 (N-CH_2), 69.3 (N-CH_2), 78.5 (CH_2NO_2), 128.8, 129.4 (CH arom), 134.2, 135.6, (Cq arom), 217.6 (CO *cis*), 222.7 (CO *trans*), 277.0 (C=Cr). MS (FAB^+): *m*/*z* 514 (28) [M^+], 486 (43) [$M^+ - CO$], 430 (10) [$M^+ - 3CO$], 402 (25) [$M^+ - 4CO$], 374 (35) [$M^+ - 5CO$], 372 (40) [$M^+ - 3CO - NO$], 356 (35) [$M^+ - 4CO - NO_2$], 323 (55) [$M^+ - Cr(CO)_5 + 1$], 289 (100), 275 (40) [$M^+ - Cr(CO)_5 - HNO_2$]. $C_{22}H_{23}ClN_2O_7Cr$ (514.8): calcd C 51.3, H 4.5, N 5.4; found C 51.5, H 4.8, N 5.2.

9b (minor diastereoisomer): yellow solid, mp 140 °C dec (diethyl ether/pentane). ^1H NMR ($CDCl_3$): δ 0.86 (d, $^3J = 7.1$ Hz, 3H, CH_{3ax}), 0.96 (d, $J = 6.7$ Hz, 3H, CH_{3eq}), 1.50 (ddd, $^2J = 13.5$ Hz, $^3J = 10.2$ Hz, $^3J = 4.4$ Hz, 1 H, CH_{ax}H), 1.60 (dt, $^2J = 13.5$ Hz, $^3J = 4.0$ Hz, 1 H, CHH_{eq}), 1.94 (m, 1 H, C*H*-CH_{3ax}), 2.21 (m, 2 H, C*H*-CH_{3eq}), 2.72 (dd, $^2J = 12.8$ Hz, $^3J = 3.0$ Hz, 1 H, N-HH_{ax}), 3.14 (dd, $^2J = 12.8$ Hz, $^3J = 8.3$ Hz, 1 H, Cr=CC*H*H), 3.34 (dd, $^2J = 12.8$ Hz, $^3J = 10.4$ Hz, 1 H, N-CHH_{ax}), 3.48 (dd, $^2J = 12.8$ Hz, $^3J = 3.7$ Hz, 1 H, N-CH_{eq}H), 3.70 (dd, $^2J = 12.8$ Hz, $^3J = 6.4$ Hz, 1H, Cr=CC*H*H), 3.83 (m, 1 H, Ph-C*H*), 4.52 (br d, $^2J = 12.8$ Hz, 1H, N-CHH_{eq}), 4.79 (dd, A part of ABX system, $^2J = 12.8$ Hz, $^3J = 4.9$ Hz, 1 H, CH*H*NO$_2$), 4.88 (dd, B part of ABX system, $^2J = 12.8$ Hz, $^3J = 10.7$ Hz, 1 H, C*H*HNO$_2$), 7.12 (d, 2 H, H arom), 7.43 (d, 2 H, H arom). ^{13}C NMR ($CDCl_3$): δ 16.9 (CH_{3ax}), 17.7 (CH_{3eq}), 28.3 (CH_3*C*H), 29.9 (CH_3*C*H), 38.6 (C-CH_2-C), 42.1 (Ph-*C*H), 53.7(*C*H_2C=Cr), 58.4 (N-CH_2), 69.6 (N-CH_2), 78.4 (CH_2NO_2), 128.8, 129.4 (CH arom), 134.3, 136.2 (Cq arom), 217.8 (CO *cis*), 222.4 (CO *trans*), 277.4 (C=Cr).

***p*-NO$_2$ 8c** (major diastereoisomer): yellow solid, mp 51−54 °C dec (diethyl ether/pentane). IR (Nujol): ν 2053 (CO *trans*), 1912 (CO *cis*), 1559, 1422 (NO_2), 1350 (NO_2 arom.) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.98 (d, $^3J = 7.0$ Hz, 3H, CH_{3ax}), 1.01 (d, $J =$ 6.7 Hz, 3H, CH_{3eq}), 1.57−1.80 (m, 2 H, C-CH_2-C), 2.28 (m, 2 H, C*H*-CH_3), 3.37 (dd, $^2J = 13.7$ Hz, $^3J = 6.9$ Hz, 1 H, Cr=CC*H*H), 3.51 (dd, $^2J = 12.9$ Hz, $^3J = 10.7$ Hz, 1 H, N-CHH_{ax}) 3.65 (dd, $^2J = 12.6$ Hz, $^3J = 3.4$ Hz, 1 H, N-CHH_{ax}), 3.76 (dd,

$^2J = 12.6$ Hz, $^3J = 8.9$ Hz, 1 H, N-CH_{eq}H), 4.00 (m + dd, $^2J = 13.7$ Hz, $^3J = 8.1$ Hz, 2 H, Cr═CCHH + Ph-CH), 4.56 (br d, $^2J = 12.9$ Hz, 1H, N-CHH_{eq}), 4.78 (m, AB part of ABX system, 2 H, CH$_2$NO$_2$), 7.36 (d, 2 H, H arom), 8.20 (d, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.5 (CH$_{3ax}$), 17.5 (CH$_{3eq}$), 27.7 (CH$_3$$C$H), 29.8 (CH$_3$$C$H), 38.2 (C−CH$_2$−C), 41.2 (Ph-$C$H), 53.3 ($CH_2$C═Cr), 58.7 (N-CH$_2$), 69.1 (N-CH$_2$), 77.5 (CH$_2NO_2$), 123.9, 128.1, (CH arom), 145.0, 148.0 (Cq arom), 217.0 (CO *cis*), 222.8 (CO *trans*), 275.0 (C═Cr). MS (FAB$^+$): m/z 497 (3) [M$^+$ − CO], 451 (2) [M$^+$ − CO − HNO$_2$], 421 (3) [M$^+$ − CO − NO$_2$ − NO], 413 (5) [M$^+$ − 4CO], 384 (5) [M$^+$ − 5CO − 1], 352 [M$^+$ − 4CO − NO$_2$], 334 (12) [M$^+$ − Cr(CO)$_5$ + 1], 287 (8) [M$^+$ − Cr(CO)$_5$ − NO$_2$], 256 (18) [M$^+$ − Cr(CO)$_5$ − NO$_2$ − HNO], 241 (10) [M$^+$ − Cr(CO)$_5$ − 2NO$_2$], 91 (100). C$_{22}$H$_{23}$N$_3$O$_9$Cr (525.43): calcd C 50.5, H 4.4, N 8.0; found C 50.6, H 4.0, N 8.0.

9c (minor diastereoisomer): yellow solid, mp 140 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 0.90 (d, $^3J = 7.0$ Hz, 3H, CH$_{3ax}$), 1.01 (d, $J = 6.7$ Hz, 3H, CH$_{3eq}$), 1.26 (m, 1 H, CHH_{ax}), 1.54 (m, 1 H, CHH_{eq}), 2.04 (m, 1 H, CH-CH$_{3ax}$), 2.26 (m, 1 H, CH-CH$_{3eq}$), 2.88 (dd, $^2J = 12.8$ Hz, $^3J = 3.2$ Hz, 1 H, N-HH_{ax}), 3.20 (dd, $^2J = 13.1$ Hz, $^3J = 7.9$ Hz, 1 H, Cr═CCHH), 3.40 (dd, $^2J = 12.7$ Hz, $^3J = 10.2$ Hz, 1 H, N-CH_{ax}H), 3.54 (br dd, $^2J = 12.8$ Hz, $^3J = 3.7$ Hz, 1 H, N-CHH_{eq}), 3.82 (dd, $^2J = 13.1$ Hz, $^3J = 7.2$ Hz, 1H, Cr═CCHH), 3.98 (m, 1 H, Ph-CH), 4.58 (br d, $^2J = 12.7$ Hz, 1H, N-CHH_{eq}), 4.86 (m, A part of ABX system, $^2J = 13.2$ Hz, $^3J = 4.8$ Hz, 2 H, CHHNO$_2$), 4.98 (m, B part of ABX system, $^2J = 13.2$ Hz, $^3J = 10.8$ Hz, 2 H, CHHNO$_2$), 7.40 (m, 2 H, H arom), 8.30 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 17.4 (CH$_{3ax}$), 18.1 (CH$_{3eq}$), 28.7 (CH$_3$$C$H), 30.7 (CH$_3$$C$H), 39.1 (C-CH$_2$-C), 42.1 (Ph-$C$H), 52.4 ($CH_2$C═Cr), 59.6 (N-CH$_2$), 70.0 (N-CH$_2$), 78.3 (CH$_2NO_2$), 124.9, 128.9, (CH arom), 144.5, 148.0 (Cq arom), 217.9 (CO *cis*), 222.8 (CO *trans*), 271.0 (C═Cr).

***p*-MeO. 9e** (major diastereoisomer): yellow solid, mp 115−117 °C dec (diethyl ether/pentane). IR (Nujol): ν 2051 (CO *trans*), 1903 (CO *cis*), 1555, 1380 (NO$_2$), 1254 (OCH$_3$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.87 (d, $^3J = 6.9$ Hz, 3H, CH$_{3ax}$), 0.97 (d, $J = 6.7$ Hz, 3H, CH$_{3eq}$), 1.46 (ddd, $^2J = 13.5$ Hz, $^3J = 10.3$ Hz, $^3J = 4.7$ Hz, 1 H, CH_{ax}H), 1.60 (br dt, $^2J = 13.5$ Hz, $^3J = 3.9$ Hz, 1 H, CHH_{eq}), 1.90 (m, 1 H, CH-CH$_{3ax}$), 2.22 (m, 1 H, CH-CH$_{3eq}$), 2.67 (dd, $^2J = 13.0$ Hz, $^3J = 2.9$ Hz, 1 H, N-HH_{ax}), 3.17 (dd, $^2J = 12.7$ Hz, $^3J = 8.7$ Hz, 1 H, Cr═CCHH), 3.30 (dd, $^2J = 12.5$ Hz, $^3J = 10.4$ Hz, 1 H, N−CHH_{ax}), 3.51 (br dd, $^2J = 13.1$ Hz, $^3J = 3.0$ Hz, 1 H, N-CH_{eq}H), 3.70 (dd, $^2J = 12.7$ Hz, $^3J = 5.9$ Hz, 1 H, Cr═CCHH), 3.80 (m, 1 H, Ph-CH), 3.82 (s, 3 H, OCH$_3$) 4.55 (br d, $^2J = 12.7$ Hz, 1H, N-CHH_{eq}), 4.80 (dd, A part of ABX system, $^2J = 12.5$ Hz, $^3J = 5.0$ Hz, 1 H, CHHNO$_2$), 4.90 (dd, B part of ABX system, $^2J = 12.6$ Hz, $^3J = 10.8$ Hz, 1 H, CHHNO$_2$), 6.86 (m, 2 H, H arom), 7.15 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.8 (CH$_{3ax}$), 17.7 (CH$_{3eq}$), 28.2 (CH$_3$$C$H), 29.7 (CH$_3$$C$H), 38.6 (C-CH$_2$-C), 41.7 (Ar-$C$H), 54.0 ($CH_2$C═Cr), 55.3 (OCH$_3$), 58.2 (N-CH$_2$), 69.5 (N-CH$_2$), 78.9 (CH$_2NO_2$), 114.6, 128.5 (CH arom), 129.0, 159.4 (Cq arom), 217.8 (CO *cis*), 222.6 (CO *trans*), 270.7 (C═Cr). MS (FAB$^+$): m/z 511 (2) [M$^+$], 426 (7) [M$^+$ − 3CO], 398 (6) [M$^+$ − 4CO], 370 (10) [M$^+$ − 5CO], 368 (14) [M$^+$ − 4CO − NO], 352 (7) [M$^+$ − 4CO − NO$_2$], 319 (15) [M$^+$ − Cr(CO)$_5$ +1], 285 (100), 272 (12) [M$^+$ − Cr(CO)$_5$ − NO$_2$]. C$_{23}$H$_{26}$N$_2$O$_8$Cr (510.46): calcd C 54.1, H 5.1, N 5.5; found C 53.8, H 5.5, N 5.7.

8e (minor diastereoisomer): yellow solid, mp 90−92 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 0.95 (d, $^3J = 6.8$ Hz, 3H, CH$_{3ax}$), 1.02 (d, $J = 6.7$ Hz, 3H, CH$_{3eq}$), 1.65 (m, 2 H, CH$_2$), 2.25 (m, 2 H, CH-CH$_3$), 3.32 (dd, $^2J = 13.3$ Hz, $^3J = 6.2$ Hz, 1 H, N-CH_{ax}H), 3.50−3.75 (m, 4 H, Cr═CCH_2 + N-CHH_{eq} + N-CH_{ax}H), 3.80 (m, 3 H, OCH$_3$), 3.89 (m, 1 H, Ph-CH), 4.50 (dd, $^2J = 13.2$ Hz, $^3J = 3.7$ Hz, 1H, N-CHH_{eq}), 4.70 (m, 2 H, CH_2NO$_2$), 6.90 (m, 2 H, H arom), 7.10 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 17.1 (CH$_{3ax}$), 17.7 (CH$_{3eq}$), 28.2 (CH$_3$$C$H), 29.8 (CH$_3$$C$H), 38.7 (C-CH$_2$-C), 41.1 (Ar-$C$H), 54.4 ($CH_2$C═Cr), 55.3 (OCH$_3$), 58.8 (N-CH$_2$), 69.0 (N-CH$_2$), 79.1 (CH$_2NO_2$), 114.6, 128.5 (CH arom), 129.3, 159.4 (Cq arom), 217.7 (CO *cis*), 222.7 (CO *trans*), 275.5 (C═Cr).

***p*-N(CH$_3$)$_2$, 9f** (major diastereoisomer): yellow solid, mp 118−120 °C dec (diethyl ether/pentane). IR (Nujol): ν 2051 (CO *trans*), 1908 (CO *cis*), 1555, 1380 (NO$_2$), cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.87 (d, $^3J = 6.9$ Hz, 3 H, CH$_{3ax}$), 0.97 (d, $J = 6.7$ Hz, 3H, CH$_{3eq}$), 1.45 (ddd, $^2J = 13.5$ Hz, $^3J = 10.2$ Hz, $^3J = 4.7$ Hz, 1 H, CH_{ax}H), 1.60 (br dt, $^2J = 13.5$ Hz, $^3J = 3.9$ Hz, 1 H, CHH_{eq}), 1.95 (m, 1 H, CH-CH$_{3ax}$), 2.23 (m, 1 H, CH-CH$_{3eq}$), 2.75 (dd, $^2J = 13.2$ Hz, $^3J = 3.2$ Hz, 1 H, N-CHH_{ax}), 2.90 (s, 6 H, N(CH$_3$)$_2$), 3.15 (dd, $^2J = 12.0$ Hz, $^3J = 8.0$ Hz, 1 H, Cr═CCHH), 3.34 (dd, $^2J = 12.6$ Hz, $^3J = 10.4$ Hz, 1 H, N-CH_{ax}H), 3.52 (br dd, $^2J = 13.2$ Hz, $^3J = 3.0$ Hz, 1 H, N-HH_{eq}), 3.70 (dd, $^2J = 12.0$ Hz, $^3J = 3.8$ Hz, 1 H, Cr═CCHH), 3.75 (m, 1 H, Ar-CH), 4.55 (br d, $^2J = 12.6$ Hz, 1H, N-CHH_{eq}), 4.75 (dd, A part of ABX system, $^2J = 12.5$ Hz, $^3J = 4.9$ Hz, 1 H, CHHNO$_2$), 4.87 (dd, B part of ABX system, $^2J = 12.5$ Hz, $^3J = 10.4$ Hz, 1 H, CHHNO$_2$), 6.70 (m, 2 H, H arom), 7.00 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 16.9 (CH$_{3ax}$), 17.7 (CH$_{3eq}$), 28.2 (CH$_3$$C$H), 29.7 (CH$_3$$C$H), 38.6 (C-CH$_2$-C), 40.3 (N(CH$_3$)$_2$), 41.7 (Ar-$C$H), 54.3 ($CH_2$C═Cr), 58.1 (N-CH$_2$), 69.5 (N-CH$_2$), 79.0 (CH$_2NO_2$), 112.7, 128.2 (CH arom), 124.4, 154.2 (Cq arom), 217.9 (CO *cis*), 222.8(CO *trans*), 270.6 (C═Cr). MS (FAB$^+$): m/z 495 (3) [M$^+$ − CO], 439 (40) [M$^+$ − 3CO], 408 (42) [M$^+$ − 3CO − HNO], 383 (12) [M$^+$ − 5CO], 337 (5) [M$^+$ − 5CO − NO$_2$], 331(5) [M$^+$ − Cr(CO)$_5$], 285 (15) [M$^+$ − Cr(CO)$_5$ − NO$_2$], 298 (100). C$_{24}$H$_{29}$N$_3$O$_7$Cr (523.50): calcd C 55.3, H 5.2, N 8.1; found C 54.5, H 5.7, N 8.5.

8f (minor diastereoisomer): yellow solid, mp 59−61 °C dec (diethyl ether/pentane). ^{1}H NMR (CDCl$_3$): δ 0.93 (d, $^3J = 6.9$ Hz, 3H, CH$_{3ax}$), 1.02 (d, $J = 6.7$ Hz, 3H, CH$_{3eq}$), 1.62 (m, 2 H, CH$_2$), 2.22 (m, 1 H, CH-CH$_{3ax}$), 2.26 (m, 1 H, CH-CH$_{3eq}$), 2.95 (s, 6 H, N(CH$_3$)$_2$), 3.33 (dd, $^2J = 13.2$ Hz, $^3J = 6.5$ Hz, 1 H, N-CH_{ax}H), 3.55−3.75 (m, 4 H, Cr═CCH_2 + N-CHH_{eq} + N-CH_{ax}H), 3.86 (m, 1 H, Ph-CH), 4.46 (dd, $^2J = 12.9$ Hz, $^3J = 3.7$ Hz, 1H, N-CHH_{eq}), 4.65 (m, AB part of ABX system, 2 H, CH_2NO$_2$), 6.68 (m, 2 H, H arom), 7.01 (m, 2 H, H arom). ^{13}C NMR (CDCl$_3$): δ 17.2 (CH$_{3ax}$), 17.8 (CH$_{3eq}$), 28.2 (CH$_3$$C$H), 29.6 (CH$_3$$C$H), 38.8 (C-CH$_2$-C), 40.3 (N(CH$_3$)$_2$), 41.2 (Ar-$C$H), 54.8 ($CH_2$C═Cr), 58.8 (N-CH$_2$), 69.0 (N-CH$_2$), 79.2 (CH$_2NO_2$), 112.9, 128.1 (CH arom), 124.4, 154.2 (Cq arom), 217.8 (CO *cis*), 222.7 (CO *trans*), 276.0 (C═Cr).

Crystallography. A suitable crystal was mounted on a glass fiber on a CAD4 diffractometer, which was used for the space group determination and for the data collection. Unit cell dimensions were obtained by least-squares fit of the 2θ values of 25 high-order reflections ($9.0° < \theta < 15.0°$). Selected crystallographic and other relevant data are listed in Supplementary Table S1.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and were measured every 90 min.; no significant variation was detected. Data were corrected for Lorentz and polarization factors using the data reduction programs of the MOLEN crystallographic package.[17] An empirical absorption correction was also applied (azimuthal (Ψ) scans of three reflections having $\chi > 85°$).[18] The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as shown in Table 8.

The structure was solved by a combination of direct and Fourier methods and refined by full-matrix least-squares minimizing the function $[\sum w(|F_o| - 1/k|F_c|)^2]$) with $w = [\sigma^2(F_o)]^{-1}$.

Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms in their

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(17) *MOLEN*, Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, The Netherlands, 1990.

(18) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A* **1968**, *24*, 351.

calculated position (C−H = 0.95 Å, $B_{iso}(H) = 1.53 \times B_{eq}(C_{bonded})$ Å^2) was taken into account but not refined.

No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[19]

Upon convergence the final Fourier difference map showed no significant peaks.

All calculations were carried out by using the Enraf-Nonius MOLEN crystallographic package.[17]

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for compound **1**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, and bond distances and angles, as well as an ORTEP figure showing the full numbering scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000795I

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(19) *International Tables for X-ray Crystallography*; Kynoch: Birmingham England, 1974; Vol. IV.