Direct Observation of Orthogonal Orientation of an Aromatic Ring Attached to the Carbene Carbon in Fischer Carbene Complexes in Solution: Diastereotopicity of Benzyl Protons as a Stereochemical Probe†

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Diastereotopicity of methylene protons of benzyloxy and benzylamino groups in Fischer carbene complexes serves as a stereochemical probe to reveal orthogonal orientation of the aromatic rings attached to the carbene carbon with respect to the metal−carbene π-plane *in solution*.

Introduction

Crystal structures of Fischer carbene complexes[1] reveal that an aryl ring attached to the carbene carbon of the complex is oriented orthogonal to the metal−carbene π-plane in solid state.[2] In a series of papers,[3] Fischer studied solution conformation of these complexes with particular reference to the barrier of rotation about the $C_{carbene}$−N or $C_{carbene}$−O bond in various structures. Restricted rotation of these bonds led to the identification of *E* and *Z* conformers[4] and definitive assignment of NMR signals for each. However, the preferred orientation of the aromatic ring with respect to the coordinated carbene plane in solution remained to be ascertained. It was observed that the chemical shift difference between the *E*- and *Z*-methoxy signals is in the range of 0.5 ppm for methylcarbene complexes. This difference was about 1.0 ppm in arylcarbene complexes (the *E*-methoxy signal was shielded, but the *Z*-methoxy signal was practically invariant). However, it was not possible to clearly attribute the shielding of the *E*-methoxy group to the anisotropy of a neighboring, orthogonal, aromatic ring. In this paper, we have used the diastereotopicity of prochiral benzyl groups[5] in a series of Fischer carbene complexes to contend that the aromatic ring indeed is oriented orthogonal[6] to the carbene plane *in solution*.

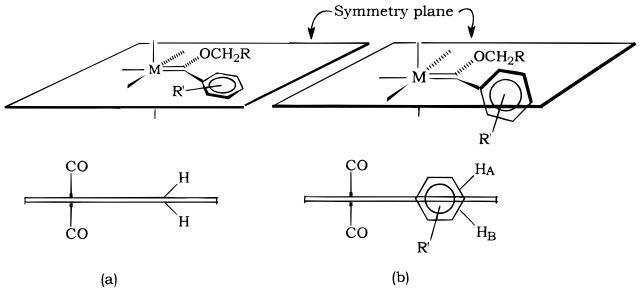

Figure 1.

Results and Discussion

The conclusion is based on a simple model often used to determine diastereotopicity of geminal groups,[5a] as shown in Figure 1. The aromatic ring attached to the carbene carbon can adopt two orientations as shown (Figure 1). In both (a) and (b), the *ipso* carbon and the *para* position of the aromatic ring are contained in the symmetry plane. In the coplanar orientation (a), the substitution pattern on the aromatic ring adds no further dimension, since they are included in the symmetry plane as well, and the prochiral benzyl protons would remain enantiotopic. For the orthogonal orientation (b), an unsymmetrical substitution pattern would destroy the symmetry of the molecule; as a consequence, the protons H_A and H_B would become diastereotopic. Thus, the AB pattern of the methylene protons of the *E*-conformer would provide a probe for orthogonality of the aromatic ring attached to the carbene carbon.[7]

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(1) For recent reviews, see: (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, Chapter 5.3. Hegedus, L. S. *Ibid*., Vol. 12, Chapter 5.4. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5.

(2) (a) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983. For the few α,β-unsaturated carbene complexes characterized by crystallography, the π-plane is found to be coplanar: Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784. Huttner, G.; Lange, S. *Chem. Ber.* **1970**, *103*, 3149.

(3) (a) Fischer, E. O.; Kreiter, C. G. Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237. (b) Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Eng.* **1969**, *8*, 761. (c) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.

(4) The *E*/*Z* nomenclature, normally used to define olefin geometries, is adopted throughout this text for convenience of unambiguous stereochemical description.

(5) (a) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307. (b) Mislow, K.; Raban, M. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1967; Vol. 1, p 1. (c) Raban, M.; Lauderback, S. K.; Kost, D. *J. Am. Chem. Soc.* **1975**, *97*, 5178.

(6) In this paper the term "orthogonal" is used throughout to denote an out-of-plane orientation in which relevant dihedral angles approach 90°.

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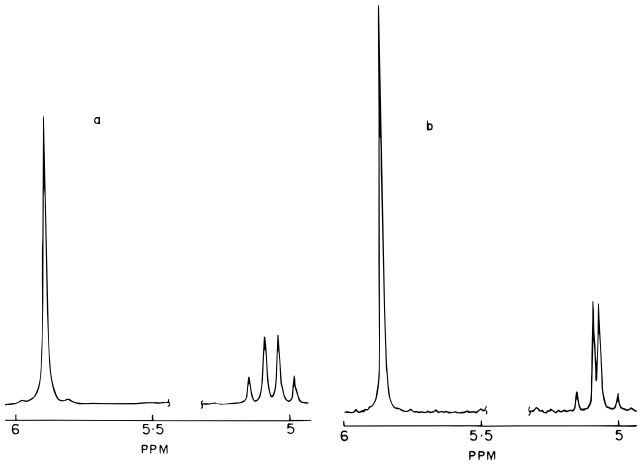
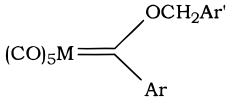


Figure 2. Low-temperature PMR spectra: (a) complex **1a** (CD_2Cl_2, −75 °C); (b) complex **1b** (CD_2Cl_2, −55 °C).

Chart 1



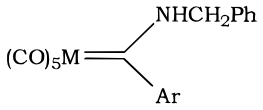
	M	Ar	Ar'	Yield (%)
1a	W	2-OMe-C_6H_4	4-OMeC_6H_4	55
1b	W	2-OMe-C_6H_4	2-Furyl	37
1c	Cr	2-OMe-C_6H_4	4-MeC_6H_4	45
1d	Cr	2-Me-C_6H_4	4-MeC_6H_4	43

Initial observations were made for structurally analogous carbene complexes **1a-d** (Chart 1). The proton NMR spectrum of the tungsten complex **1a** at room temperature showed a broad signal at 5.5 ppm due to the methylene protons. On cooling, the signal decoalesced, and at −75 °C two sharp signals of different multiplicity were obtained (Figure 2a). The broad singlet was assigned to the *Z*-conformer and the four-line AB pattern to the E-conformer on the basis of precedents.[8]

Similar observation was made for the tungsten complex **1b** as well (Figure 2b). There is a subtle difference in the line shape of the benzylic protons corresponding to the *E*-conformer of these complexes. Similar peak multiplicities were also observed in the low-temperature ^{1}H NMR spectra of chromium complexes **1c**,**d**. The benzylic methylene signal of the *Z*-conformer in all these cases remained a broad singlet. However, expected peak multiplicity of this signal was observed in the aminocarbene complexes (*vide infra*).

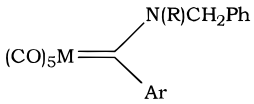
Since aminocarbene complexes have a higher barrier to rotation of the $C_{carbene}$−N bond, we expected that similar distinction between features of the *E*- and the *Z*-conformers should be discernible in their NMR spectra at room temperature, thereby avoiding variable-temperature experiments. The spectra of structurally related aminocarbene complexes (Charts 2 and 3) indeed showed the presence of two conformers at ambient temperature.

Chart 2



	M	Ar	Yield (%)
2a	Cr	2-MeC_6H_4	92
2b	Cr	2-OMeC_6H_4	96
2c	Cr	3-MeC_6H_4	98
2d	Cr	3-OMeC_6H_4	89
2e	Cr	4-OMe-3-MeC_6H_3	89
2f	Cr	4-MeC_6H_4	93
2g	Cr	1-Naphthyl	95
2h	Cr	C_6H_5	97
2i	W	2-OMeC_6H_4	89
2j	W	3-MeC_6H_4	97

Chart 3



	M	Ar	R	Yield (%)
3a	Cr	2-MeC_6H_4	Me	87
3b	Cr	2-MeC_6H_4	$CH_2C_6H_5$	93
3c	Cr	2-OMeC_6H_4	$CH_2C_6H_5$	89
3d	Cr	2-OMeC_6H_4	Me	93
3e	Cr	3-MeC_6H_4	$CH_2C_6H_5$	91
3f	Cr	3-OMeC_6H_4	$CH_2C_6H_5$	97
3g	Cr	4-OMe-3-MeC_6H_3	$CH_2C_6H_5$	88
3h	Cr	4-MeC_6H_4	$CH_2C_6H_5$	91
3i	Cr	C_6H_5	$CH_2C_6H_5$	87
3j	Cr	1-Naphthyl	$CH_2C_6H_5$	84
3k	W	2-OMeC_6H_4	$CH_2C_6H_5$	93
3l	W	3-MeC_6H_4	$CH_2C_6H_5$	97

Representative spectral patterns are reproduced in Figure 3. The pattern in Figure 3a depicts an accidental degeneracy of the nonequivalent benzyl protons of complex **2b** in $CDCl_3$. The degeneracy is lifted by the use of a different solvent like C_6D_6 (Figure 3b). The chromium carbene complex **2a,** however, did not show any such degeneracy in $CDCl_3$ (Figure 3c). The benzylic proton signal corresponding to the *Z*-conformer in these complexes did not show multiplicity typical of an AB system. In a more sterically congested structure, as in the complexes **3a**,**d**, both the *Z*- and *E*-conformers exhibit doublets due to each of the benzylic protons (Figure 3d). The chemical shift nonequivalence is most accentuated in the spectra of the dibenzylamino deriva-

(7) In this model, the alkoxy group is placed *anti* with respect to the metal fragment (*E* conformer) for the sake of clarity in the diagram. For the conformation where the alkoxy group is placed *syn* to the metal fragment (*Z* conformer), the situation will still hold, but the effect may be differently manifested (*vide infra*).

(8) (a) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599. (b) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275.

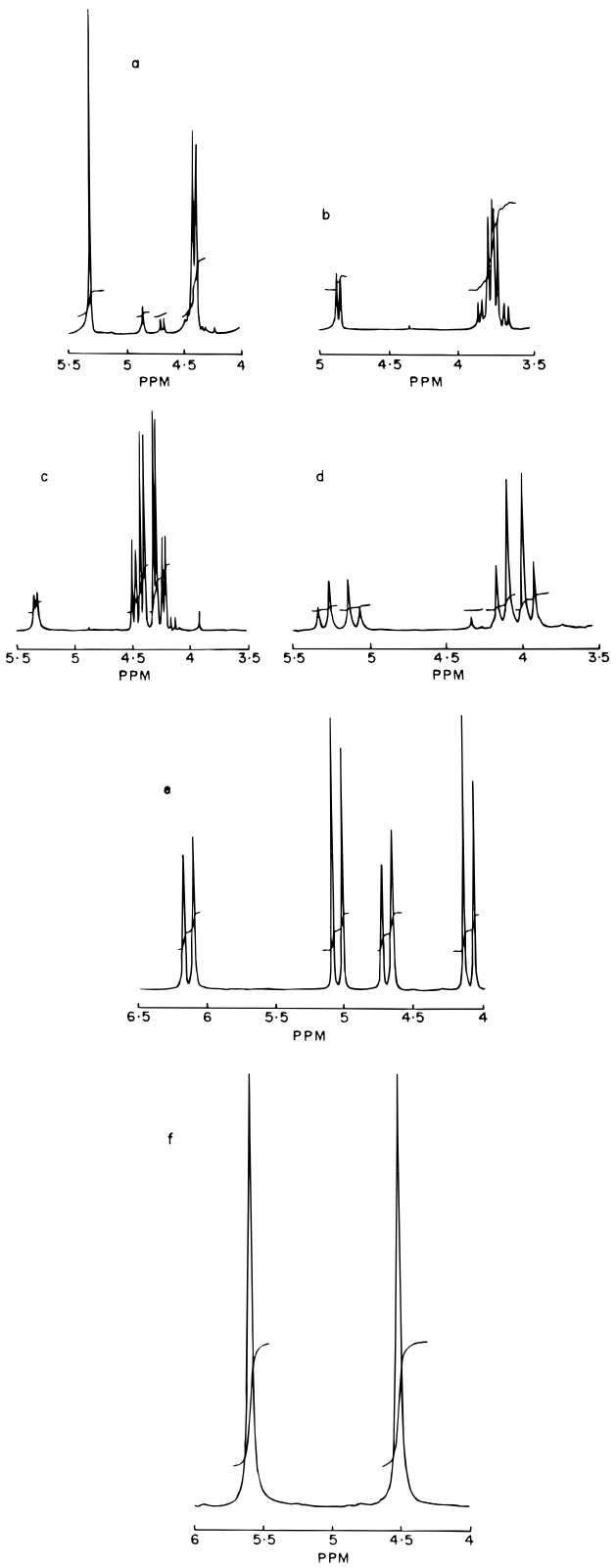


Figure 3. PMR spectra: (a) complex **2b** ($CDCl_3$); (b) complex **2b** (C_6D_6); (c) complex **2a** ($CDCl_3$); (d) complex **3d** ($CDCl_3$); (e) complex **3b** ($CDCl_3$); (f) complex **3h** ($CDCl_3$).

tives **3b**,**c**,**k** (Figure 3e). Heating a related complex **3c** in toluene-d_8 to 70 °C in the NMR probe did not result in any broadening of peaks indicating that rotation of the bond between the *ipso*-carbon of the aromatic ring and the carbene carbon has a high rotation barrier[9] and as such does not interfere with present interpretations.

Assignment of signals due to the methylene protons

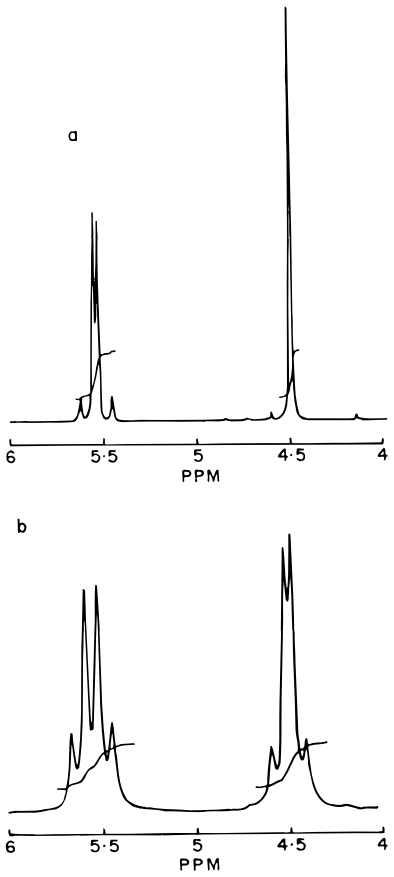


Figure 4. PMR spectra: (a) complex **3f** ($CDCl_3$); (b) complex **3g** ($CDCl_3$).

of the *E*- and *Z*-benzylic groups were based on 2D experiments. That this nonequivalence of geminal protons had arisen because of an unsymmetrically substituted aromatic ring attached to the carbene carbon was evident from the sprectrum of complex **3h** (Figure 3f) where the aromatic ring was substituted at the *para* position only; two singlets are obtained for the *E*- and *Z*-benzylic protons. The same pattern was observed for complex **3i**, which contained an unsubstituted phenyl ring. However, the chemical shift difference between the *E*- and *Z*-benzylic protons remained the same, indicating no significant change of conformation in these complexes.

The dissymmetry imposed by a *meta*-substituent was reflected in the spectra of the amino carbene complexes **2c**−**e** and **3e**−**g**. In the benzylamino complexes **2c**−**e** the nonequivalent geminal protons of the benzyl group showed degeneracy in both $CDCl_3$ and C_6D_6. Degeneracy was lifted for the dibenzylamino complexes **3f**,**g** (Figure 4).

Interestingly, the benzylic protons of the *Z*-conformer showed a four-line pattern in the spectrum of the complex **3f**, while the corresponding protons of the *E*-conformer remained degenerate. Normally the opposite trend was observed in the case of *ortho*-substituted aryl (benzyloxy)- and (benzylamino)carbene complexes. This also suggests that the usual appearance of a broad singlet for the *Z*-conformer is the result of relatively small $\Delta\Delta\nu$ for the diastereotopic protons rather than a reflection of signal averaging due to fast rotation about the bond between aromatic *ipso*-carbon

and the carbene carbon.[9] For the complex **3g**, both the *syn* and *anti* benzyl protons displayed four-line patterns, as expected—the *p*-OMe group on the aromatic ring does not appear to enforce a planar orientation in this complex.[10]

Conclusion

The diastereotopicity of benzyl protons thus provided a useful internal probe to ascertain the conformation of Fischer carbene complexes[11] as they exist *in solution*. The results, in essence, supplement the observations made for their solid-state structures.

Experimental Section

All reactions were performed under an inert atmosphere of argon. Ether, benzene, and toluene were dried over sodium and freshly distilled from sodium−benzophenone ketyl under argon. Dichloromethane was distilled over P_2O_5 under argon. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer as chloroform solutions. The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer whereas ^{13}C NMR spectra were recorded on Bruker AC-200 and MSL-300 spectrometers at 50.3 and 75.5 MHz, respectively, using $CDCl_3$ as the solvent, unless otherwise mentioned, and reported as parts per million downfield of tetramethylsilane. NMR spectra of the *E*- and *Z*-isomers were assinged on the basis of relative intensities. Elemental analyses of solid compounds were carried out on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL. The liquid samples did not give satisfactory elemental analyses. Melting points in the Celsius scale were determined in open capillary tubes on a Thermonik Campbell melting point apparatus and are uncorrected. All ((arylmethyl)oxy)arylcarbene complexes undergo rearrangement at the range of their melting points (70−110 °C) and could not be recorded.

All reagents were purchased from Aldrich and used as received.

General Procedure for the Preparation of ((Arylmethyl)oxy)arylcarbene Complexes 1a−d. The complexes were prepared essentially by following a literature procedure.[13] To a solution of tetraethylammonium pentacarbonyl(1-oxyalkylidene)metalate(0) (*n* mmol) in dichloromethane (5*n* mL) was added freshly distilled acetyl chloride (1.2*n* mmol) dropwise at −40 °C. After the solution was stirred for 1 h, alcohol (1.2*n* mmol) was added dropwise at −40 °C and the reaction mixture was stirred at −20 °C for 2 h and then at 0 °C for 2−3 h. The solvent was evaporated under reduced pressure. The residue was extracted in petroleum ether, and the combined extract was concentrated under reduced pressure. The residue was flash chromatographed using 10% dichloromethane/petroleum ether as the eluant.

Complex 1a: Red solid, *E:Z* = 37:63. IR: 2030 (m), 1990 (sh), 1940 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −75 °C): *E*-**1a**, δ 3.89 (s, 3H), 3.82 (s, 3H), 5.00 (d, J = 12 Hz, 1H), 5.13 (d, J = 12 Hz, 1H); *Z*-**1a**, δ 3.79 (s, 3H), 3.82 (s, 3H), 5.88 (s, 2H); combined peaks, δ 6.78−7.61 (m, 8H and 8H). ^{13}C NMR (room temperature): δ 55.51, 83.48, 111.28, 114.38, 120.39, 122.15, 126.56, 130.00, 130.20, 150.11, 160.43, 197.49, 205.88, 325.17. Anal. Calcd for $C_{21}H_{16}O_8W$: C, 46.06; H, 2.92. Found: C, 46.37; H, 3.21.

Complex 1b: Red solid, *E:Z* = 42:58. IR: 2025 (m), 1985 (sh), 1930 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −55 °C): *E*-**1b**, δ 3.90 (s, 3H), 5.03 (d, J = 12 Hz, 1H), 5.12 (d, J = 12 Hz, 1H); *Z*-**1b**, δ 3.80 (s, 3H), 5.87 (s, 2H); combined peaks, δ 6.46−7.62 (m, 7H and 7H). ^{13}C NMR (room temperature): δ 19.14, 76.32, 111.15, 112.66, 122.57, 125.48, 127.39, 128.73, 130.85, 144.55, 147.64, 197.04, 204.59, 330.25. Anal. Calcd for $C_{18}H_{12}O_8W$: C, 40.00; H, 2.22. Found: C, 40.10; H, 2.43.

Complex 1c: Red solid, *E:Z* = 95:5. IR: 2040 (m), 1970 (sh), 1940 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −55 °C): *E*-**1c**, δ 2.43 (s, 3H), 3.89 (s, 3H), 5.12 (d, J = 14 Hz, 1H), 5.23 (d, J = 14 Hz, 1H); *Z*-**1c**, δ 2.46 (s, 3H), 3.81 (s, 3H), 6.15 (s, 2H); combined peaks, δ 6.70−7.62 (m, 8H and 8H). ^{13}C NMR (room temperature): δ 21.41, 55.50, 80.83, 111.20, 120.94, 121.56, 128.21, 129.62, 129.95, 131.86, 138.92, 141.26, 148.86, 216.36, 225.58, 353.00. Anal. Calcd for $C_{21}H_{16}O_7Cr$: C, 58.33; H, 3.70. Found: C, 58.49; H, 4.12.

Complex 1d: Red solid, *E:Z* = 85:15. IR: 2050 (m), 1990 (sh), 1950 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −55 °C): *E*-**1d**, δ 2.17 (s, 3H), 2.37 (s, 3H), 4.95 (d, J = 13 Hz, 1H), 5.07 (d, J = 13 Hz, 1H); *Z*-**1d**, δ 2.00 (s, 3H), 2.37 (s, 3H), 6.10 (s, 2H); combined peaks, δ 6.80−7.50 (m, 8H and 8H). ^{13}C NMR (room temperature): δ 19.14, 21.46, 81.20, 120.75, 126.12, 126.42, 128.44, 129.76, 130.88, 131.41, 139.28, 152.57, 216.31, 224.82, 357.63. Anal. Calcd for $C_{21}H_{16}O_6Cr$: C, 60.58; H, 3.85. Found: C, 61.32; H, 3.91.

General Procedure for the Preparation of Alkoxyarylcarbene Complexes. All methoxy- or ethoxycarbene complexes were prepared according to the procedure of Hoye[14] starting from tetraethylammonium carbene salt and methyl iodide or ethyl iodide, respectively, using tetrabutylammonium bromide as the phase transfer catalyst and dichloromethane as the solvent.

[(2-Methylphenyl)(methoxy)methylene]pentacarbonylchromium(0): Red liquid. IR: 2085 (m), 2000 (sh), 1955 (s) cm^{-1}. ^{1}H NMR: δ 2.20 (s, 3H), 4.30 (s, 3H), 6.80−7.00 (m, 1H), 7.07−7.45 (m, 3H). ^{13}C NMR: δ 18.72, 65.64, 120.63, 126.05, 126.37, 128.41, 130.84, 152.66, 216.21, 224.70, 359.84.

[(3-Methylphenyl)(methoxy)methylene]pentacarbonylchromium(0): Red liquid. IR: 2055 (m), 1985 (sh), 1935 (s) cm^{-1}. ^{1}H NMR: δ 2.43 (s, 3H), 4.70 (s, 3H), 7.01−7.45 (m, 4H). ^{13}C NMR: δ 21.66, 67.20, 120.66, 123.22, 128.32, 131.22, 138.21, 154.12, 216.49, 224.47, 351.85.

[(3-Methylphenyl)(methoxy)methylene]pentacarbonyltungsten(0): Red solid, mp 64 °C. IR: 2080 (m), 1980 (sh), 1935 (s) cm^{-1}. ^{1}H NMR: δ 2.44 (s, 3H), 4.78 (s, 3H), 7.25−7.48 (m, 4H). ^{13}C NMR: δ 21.60, 70.28, 124.33, 126.56, 128.21, 132.73, 138.05, 155.62, 197.59, 203.86, 322.76. Anal. Calcd for $C_{14}H_{10}O_6W$: C, 36.71; H, 2.20. Found: C, 36.51; H, 2.10.

[(4-Methoxy-3-methylphenyl)(ethoxy)methylene]-pentacarbonylchromium(0): Red solid, mp 87 °C. IR: 2055 (m), 1985 (sh), 1935 (s) cm^{-1}. ^{1}H NMR: δ 1.74 (t, J = 7 Hz, 3H), 2.27 (s, 3H), 3.92 (s, 3H), 5.15 (q, J = 7 Hz, 2H), 6.87 (d, J = 8 Hz, 1H), 7.45 (s, 1H), 7.72 (dd, J = 1 and 8 Hz, 1H). ^{13}C NMR: δ 15.34, 16.48, 55.59, 77.09, 108.97, 126.23, 128.64,

(9) The rotation barrier of the bond between the *ipso* carbon of the aromatic ring and the carbonyl carbon in *ortho*-substituted aromatic ketones or amides are estimated to be 16−20 kcal/mol or more, see: (a) Oki, M. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1983; Vol. 14, p 1. (b) Sternhell, S. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 163. (c) Stewart, W. E.; Siddall, T. H., III. *Chem. Rev.* **1970**, *70*, 517. Consequently, the rotation of the bond between *ipso* carbon of the aromatic ring and carbene carbon is assumed to be slow on the NMR time scale throughout the temperature range used in the present study.

(10) An electron-donating substituent such as OMe or NMe_2 at the *para* position of the aromatic ring considerably lowers the barrier to rotation about the $C_{carbene}$−O bond in alkoxy complexes. Fischer suggested[3a] that such a phenomenon might result from a planar aromatic ring effectively donating electron density toward the carbene carbon and thus reducing the resonance contribution from oxygen lone pair.

(11) A close parallel of this observation can be drawn with the ^{1}H NMR spectra of hindered amides such as *N,N*-dibenzylamide of *o*-toluic acid,[12] where the low-temperature ^{1}H NMR spectrum reveals eight lines (four doublets) for the four benzylic protons. In this molecule, the aryl ring of the *ortho*-toluyl group is twisted out of the amide plane.

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(13) (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368. (b) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Chem. Commun*. **1971**, 570.

(14) Hoye, T. R.; Chen, K.; Vyvyan, J. R. *Organometallics* **1993**, *12*, 2806.

128.84, 146.03, 161.66, 217.25, 224.18, 339.14. Anal. Calcd for $C_{16}H_{14}O_7Cr$: C, 51.90; H, 3.81. Found: C, 52.01; H, 3.62.

General Procedure for the Preparation of Aminocarbene Complexes 2a−j. All aminocarbene complexes were prepared according to the literature procedure[15] starting from the corresponding methoxycarbene complexes and benzylamine using diethyl ether as the solvent.

Complex 2a: Yellow liquid, *E*:*Z* = 93:7. IR: 2050 (m), 1985 (sh), 1930 (s) cm^{-1}. ^1H NMR: *E*-**2a**, δ 2.27 (s, 3H), 4.27 (dd, J = 5.2 and 15.2 Hz, 1H), 4.42 (dd, J = 6.3 and 15.2 Hz 1H), 6.88 (d, J =7.6 Hz, 1H), 9.38 (bs, 1H); *Z*-**2a**, δ 2.22 (s, 3H), 5.32 (d, J = 5.2 Hz, 2H), 6.96 (d, J = 7.6 Hz, 1H), 8.68 (bs, 1H); combined peaks, δ 7.13−7.95 (m, 8H and 8H). ^{13}C NMR: *E*-**2a**, δ 19.08, 54.89, 119.91, 126.38, 127.25, 127.92, 128.91, 129.52, 130.89, 134.38, 134.75, 148.79, 217.28, 223.33, 284.34.

Complex 2b: Yellow liquid, *E*:*Z* = 87:13. IR: 2055 (m), 1975 (sh), 1930 (s) cm^{-1}. ^1H NMR (C_6D_6): *E*-**2b**, δ 3.37 (s, 3H), 3.69 (dd, J = 5.8 and 14.8 Hz, 1H), 3.82 (dd, J = 5.8 and 14.8 Hz, 1H), 6.52 (d, J = 7.8 Hz, 1H), 8.96 (bs, 1H); *Z*-**2b**, δ 3.44 (s, 3H), 4.88 (d, J = 5.8 Hz, 2H), 7.76 (bs, 1H); combined peaks, 6.70−7.40 (m, 9H). ^{13}C NMR: *E*-**2b**, δ 55.11, 55.29, 111.06, 120.84, 127.98, 128.48, 128.54, 128.87, 129.33, 134.79, 138.03, 149.05, 217.51, 223.79, 280.26; *Z*-**2b**, δ 55.11, 57.79, 64.84, 111.38, 120.42, 121.91, 127.62, 128.18, 128.69, 132.26, 143.13, 150.15, 217.51, 223.89, 278.52.

Complex 2c: Yellow liquid, *E*:*Z* = 58:42. IR: 2080 (m), 1995 (sh), 1950 (s) cm^{-1}. ^1H NMR (C_6D_6): *E*-**2c**, δ 2.07 (s, 3H), 3.68 (d, J = 5.8 Hz, 2H), 8.94 (bs, 1H); *Z*-**2c**, δ 2.12 (s, 3H), 4.87 (d, J = 5.8 Hz, 2H), 7.91 (bs, 1H); combined peaks, δ 6.43−8.11 (m, 9H and 9H). ^{13}C NMR: *E*-**2c**, δ 21.60, 54.76, 116.43, 119.88, 135.06, 138.59, 149.71, 217.44, 223.69, 282.27; *Z*-**2c**, δ 21.49, 57.97, 118.42, 121.76, 134.72, 138.34, 155.18, 217.51, 223.96, 278.68; combined peaks, δ 127.59, 127.71, 128.48, 128.95, 129.40, 129.81.

Complex 2d: Yellow liquid, *E*:*Z* = 74:26. IR: 2080 (m), 1970 (sh), 1910 (s) cm-^{1}. ^1H NMR (C_6D_6): *E*-**2d**, δ 3.30 (s, 3H), 3.70 (d, J = 6.2 Hz, 2H), 8.95 (bs, 1H); *Z*-**2d**, δ 3.40 (s, 3H), 4.85 (d, J = 6.2 Hz, 2H)), 7.95 (bs, 1H); combined peaks, δ 6.15−7.40 (m, 9H and 9H). ^{13}C NMR: *E*-**2d**, δ 55.00, 55.44, 105.27, 111.60, 112.55, 134.82, 150.83, 159.92, 217.37, 223.56, 282.44; *Z*-**2d**, δ 55.44, 58.10, 107.40, 113.37, 113.54, 134.55, 156.35, 159.57, 217.37, 223.88, 278.68; combined peaks, δ 127.68, 128.66, 128.83, 129.23, 129.52, 130.00, 130.29. Anal. Calcd for $C_{20}H_{15}NO_6Cr$: C, 57.56; H, 3.62; N, 3.36. Found: C, 57.29; H, 3.48; N, 3.29.

Complex 2e: Yellow liquid, *E*:*Z* = 61:39. IR: 2050 (m), 1980 (sh), 1928 (s) cm^{-1}. ^1H NMR (C_6D_6): *E*-**2e**, δ 2.23 (s, 3H), 3.30 (s, 3H), 3.76 (d, J = 4.9 Hz, 2H), 8.96 (bs, 1H); *Z*-**2e**, δ 2.23 (s, 3H), 3.34 (s, 3H), 4.91 (d, J = 4.9 Hz, 2H), 7.95 (bs, 1H); combined peaks, 6.28−7.70 (m, 8H and 8H). ^{13}C NMR: *E*-**2e**, δ 16.36, 54.68, 55.36, 109.78, 118.50, 122.40, 134.91, 142.02, 156.86, 217.39, 223.50, 283.54; *Z*-**2e**, δ 16.36, 55.36, 57.93, 109.57, 120.96, 124.59, 134.70, 147.96, 157.95, 217.57, 223.79, 277.60; combined peaks, δ 126.88, 127.09, 127.48, 128.54, 128.97, 129.35.

Complex 2f: Yellow liquid, *E*:*Z* = 59:41. IR: 2050 (m), 1970 (sh), 1920 (s) cm^{-1}. ^1H NMR: *E*-**2f**, δ 2.39 (s, 3H), 4.43 (d, J = 5.8 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 9.31 (bs, 1H), *Z*-**2f**, δ 2.35 (s, 3H), 5.30 (d, J = 5.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 8.73 (bs, 1H), combined peaks, δ 7.07−7.60 (m, 7H and 7H). ^{13}C NMR: *E*-**2f**, δ 21.16, 54.78, 119.53, 134.87, 136.95, 146.99, 217.45, 223.74, 283.02, *Z*-**2f**, δ 21.16, 58.03, 121.53, 134.67, 138.14, 152.71, 217.57, 224.03, 278.67; combined peaks, δ 127.62, 128.56, 128.70, 129.24, 129.42.

Complex 2g: Yellow liquid, *E*:*Z* = 73:27. IR: 2055 (m), 1980 (sh), 1920 (s) cm^{-1}. ^1H NMR: *E*-**2g**, δ 4.20 (dd, J = 4.8 and 15 Hz, 1H), 4.35 (dd, J = 5.8 and 15 Hz, 1H), 9.55 (bs, 1H); *Z*-**2g**, δ 5.45 (d, J = 4.8 Hz, 2H), 8.90 (bs, 1H); combined peaks, δ 6.95−8.25 (m, 12H and 12H). ^{13}C NMR: *E*-**2g**, δ 55.46, 117.15, 146.54, 217.25, 223.51, 283.84; *Z*-**2g**, δ 58.27, 117.95, 151.14, 217.25, 223.76, 282.32; combined peaks, 124.31, 124.47, 125.04, 125.45, 125.99, 126.47, 126.77, 127.00, 127.43, 127.58, 127.91, 128.59, 128.88, 129.07, 129.44, 129.89, 133.63, 133.81, 134.32.

Complex 2i: Yellow solid, mp 97 °C, *E*:*Z* = 30:70. IR: 2070 (m), 1985 (sh), 1930 (s) cm^{-1}. ^1H NMR (C_6D_6): *E*-**2i**, δ 3.32 (s, 3H), 3.62 (dd, J = 5.9 and 14.5 Hz, 1H), 3.74 (dd, J = 5.9 and 14.5 Hz, 1H), 8.77 (bs, 1H); *Z*-**2i**, δ 3.35 (s, 3H), 4.71 (d, J = 5.9 Hz, 2H), 7.52 (bs, 1H); combined peaks, δ 6.30−6.51 (m, 1H and 1H), 6.65−7.17 (m, 8H and 8H). ^{13}C NMR: *E*-**2i**, δ 54.92, 55.35, 111.09, 120.84, 121.53, 134.56, 138.45, 149.51, 198.71, 204.47, 258.43; *Z*-**2i**, δ 55.35, 59.82, 111.23, 120.35, 122.78, 134.56, 143.26, 150.78, 198.27, 204.39, 257.66; combined peaks, δ 128.03, 128.41, 128.74, 128.90 128.98, 129.34. Anal. Calcd for $C_{20}H_{15}O_6$ NW: C, 43.74; H, 2.75; N, 2.55. Found: C, 43.51; H, 2.70; N, 2.50.

Complex 2j: Yellow liquid, *E*:*Z* = 33:67. IR: 2070 (m), 1985 (sh), 1935 (s) cm-^{1}. ^1H NMR: *E*-**2j**, δ 2.40 (s, 3H), 4.38 (d, J = 5.4 Hz, 2H), 9.17 (bs, 1H); *Z*-**2j**, δ 2.37 (s, 3H), 5.15 (d, J = 5.4 Hz, 2H), 8.60 (bs, 1H); combined peaks, δ 6.70−7.92 (m, 9H). ^{13}C NMR: *E*-**2j**, δ 21.59, 54.51, 116.91, 120.40, 134.71, 138.40, 150.10, 198.61, 204.33, 260.90; *Z*-**2i**, δ 21.48, 60.05, 119.24, 122.59, 134.44, 138.27, 155.23, 198.27, 204.03, 258.43; combined peaks, δ 127.62, 127.98, 128.17, 128.41, 128.94, 129.13, 129.28, 129.38.

General Procedure for the Preparation of (Dialkylamino)carbene Complexes 3a−l. N-Alkylation of aminocarbene complexes was performed using a biphasic condition developed in our laboratory for C-alkylation.[16] The carbene complex (*n* mmol) in dichloromethane was treated with tetrabutylammonium bromide (0.1*n* mmol), 50% aqueous NaOH, and the halide (1.5*n* mmol). The mixture was stirred at room temperature under argon until the starting material was consumed (TLC, 1−3 h). The reaction mixture was diluted with water, extracted with dichloromethane, and concentrated under reduced pressure. The pure product was isolated by flash chromatography.

Complex 3a: Yellow solid, mp 98 °C, *E*:*Z* = 6:94. IR: 2050 (m), 1975 (sh), 1930 (s) cm^{-1}. ^1H NMR: *E*-**3a**, δ 2.16 (s, 3H), 3.88 (s, 3H), 4.19 (d, J = 14.6 Hz, 1H), 4.98 (d, J = 14.6 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H); *Z*-**3a**, δ 2.18 (s, 3H), 3.86 (s, 3H), 5.49 (d, J = 14.6 Hz, 1H), 5.72 (d, J = 14.6 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H); combined peaks, δ 7.07−7.34 (m, 3H), 7.41−7.56 (m, 5H). ^{13}C NMR: *Z*-**3a**, δ 19.23, 42.49, 67.52, 119.76, 125.70, 126.53, 126.60, 127.93, 128.99, 129.56, 131.16, 134.32, 152.25, 217.14, 223.64, 279.01. Anal. Calcd for $C_{21}H_{17}NO_5Cr$: C, 60.73; H, 4.13; N, 3.37. Found: C, 60.60; H, 4.17; N, 3.45.

Complex 3b: Yellow solid, mp 93 °C. IR: 2050 (m), 1980 (sh), 1925 (s) cm^{-1}. ^1H NMR: δ 2.31 (s, 3H), 4.10 (d, J = 14.8 Hz, 1H), 4.69 (d, J = 14.8 Hz, 1H), 5.05 (d, J = 14.8 Hz, 1H), 6.12 (d, J = 14.8 Hz, 1H), 6.88−7.60 (m, 14H). ^{13}C NMR: δ 19.93, 56.82, 64.22, 120.59, 125.89, 126.23, 126.71, 127.75, 128.60, 128.70, 129.09, 129.38, 129.46, 131.06, 133.66, 134.15, 151.80, 217.14, 223.64, 281.71. Anal. Calcd for $C_{27}H_{21}NO_5Cr$: C, 65.99; H, 4.31; N, 2.85. Found: C, 66.20; H, 4.50; N, 3.20.

Complex 3c: Yellow solid, mp 108 °C. IR: 2040 (m), 1975 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 3.96 (s, 3H), 4.39 (d, J = 14.6 Hz, 1H), 4.65 (d, J = 14.6 Hz, 1H), 5.30 (d, J = 14.6 Hz, 1H), 5.86 (d, J = 14.6 Hz, 1H), 6.89−7.18 (m, 5H), 7.18−7.32 (m, 1H), 7.32−7.64 (m, 8H). ^{13}C NMR: δ 55.14, 57.74, 63.36, 111.00, 120.87, 121.28, 127.73, 127.87, 128.42, 128.55, 129.19, 134.28, 134.47, 141.28, 148.24, 217.34, 224.08, 277.84. Anal. Calcd for $C_{27}H_{21}NO_6Cr$: C, 63.91; H, 4.17; N, 2.76. Found: C, 64.10; H, 4.40; N, 2.90.

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Complex 3d: Yellow solid, mp 90 °C, *E*:*Z* = 76:24. IR: 2070 (m), 1975 (sh), 1925 (s) cm^{-1}. ^1H NMR: ***E*-3d**, δ 3.32 (s, 3H), 3.36 (s, 3H), 3.95 (d, J = 14.5 Hz, 1H), 4.12 (d, J = 14.5 Hz, 1H); ***Z*-3d**, δ 2.26 (s, 3H), 3.38 (s, 3H), 5.10 (d, J = 14.5 Hz, 1H), 5.30 (d, J = 14.5 Hz, 1H); combined peaks, δ 6.50 (t, J = 7.8 Hz, 1H and 1H), 6.63−7.35 (m, 8H and 8H). ^{13}C NMR: ***E*-3d**, δ 48.30, 55.11, 61.82, 111.05, 120.83, 127.75, 129.24, 134.26, 141.15, 148.56, 217.69, 224.43, 275.04; ***Z*-3d**, δ 42.77, 55.28, 67.33, 111.05, 121.04, 127.58, 128.46, 134.53, 141.61, 148.12, 217.29, 224.81, 274.61. Anal. Calcd for $C_{21}H_{17}NO_6Cr$: C, 58.47; H, 3.97; N, 3.25. Found: C, 58.68; H, 4.18; N, 3.05.

Complex 3e: Yellow solid, mp 150 °C. IR: 2060 (m), 1985 (sh), 1935 (s) cm^{-1}. ^1H NMR: δ 2.37 (s, 3H), 4.48 (s, 2H), 5.55 (s, 3H), 6.60−6.82 (m, 2H), 6.90−7.15 (m, 3H), 7.18−7.65 (m, 9H). ^{13}C NMR: δ 21.87, 57.73, 63.43, 116.35, 119.90, 126.94, 127.33, 127.68, 128.49, 128.69, 128.85, 129.39, 129.49, 134.37, 138.62, 152.84, 217.29, 224.06, 280.85. Anal. Calcd for $C_{27}H_{21}NO_5Cr$: C, 62.30; H, 4.04; N, 2.69. Found: C, 62.49; H, 4.10; N, 2.68.

Complex 3f: Yellow liquid. IR: 2065 (m), 1975 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 3.80 (s, 3H), 4.50 (s, 2H), 5.48 (d, J = 14.3 Hz, 1H), 5.56 (d, J = 14.3 Hz, 1H), 6.40−6.56 (m, 2H), 6.65−6.75 (m, 1H), 6.97−7.12 (m, 2H), 7.23−7.57 (m, 9H). ^{13}C NMR: δ 55.35, 57.78, 63.42, 105.36, 111.62, 127.19, 127.59, 128.46, 128.85, 129.42, 130.14, 134.27, 153.88, 159.73, 217.25, 223.97, 279.87.

Complex 3g: Yellow solid, mp 116 °C. IR: 2050 (m), 1980 (sh), 1935 (s) cm^{-1}. ^1H NMR: δ 2.25 (s, 3H), 3.84 (s, 3H), 4.41 (d, J = 14.8 Hz, 1H), 4.60 (d, J = 14.8 Hz, 1H), 5.46 (d, J = 14.8 Hz, 1H), 5.62 (d, J = 14.8 Hz, 1H), 6.55−6.89 (m, 3H), 6.94-7.14 (m, 2H), 7.21−7.72 (m, 8H). ^{13}C NMR: δ 16.52, 55.61, 57.89, 63.68, 110.18, 117.88, 122.19, 127.35, 127.76, 128.46, 128.84, 129.39, 129.47, 134.62, 146.31, 156.23, 217.48, 224.21, 282.44. Anal. Calcd for $C_{28}H_{23}NO_6Cr$: C, 64.49; H, 4.45; N, 2.69. Found: C, 64.32; H, 4.63; N, 2.76.

Complex 3h: Yellow solid, mp 98 °C. IR: 2060 (m), 1955 (sh), 1915 (s) cm^{-1}. ^1H NMR: δ 2.39 (s, 3H), 4.48 (s, 2H), 5.58 (s, 2H), 6.90 (d, J = 7.5 Hz, 2H), 7.01−7.18 (m, 2H), 7.22 (d, 7.5 Hz, 2H), 7.34−7.72 (m, 8H). ^{13}C NMR: δ 21.15, 57.53, 63.36, 119.22, 127.22, 127.58, 128.44, 128.80, 129.32, 129.41, 134.20, 134.32, 135.85, 150.37, 217.27, 224.10, 281.06. Anal. Calcd for $C_{27}H_{21}NO_5Cr$: C, 65.99; H, 4.30; N, 2.85. Found: C, 65.56; H, 4.30; N, 2.64.

Complex 3i: Yellow solid, mp 100 °C. IR: 2040 (m), 1980 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 4.48 (s, 2H), 5.55 (s, 2H), 6.90 (d, J = 7.8 Hz, 2H), 7.00−7.65 (m, 13H). ^{13}C NMR: δ 57.41, 63.08, 118.89, 125.90, 126.88, 127.27, 128.15, 128.44, 129.03, 129.12, 133.80, 133.90, 152.45, 216.86, 223.68, 280.15. Anal. Calcd for $C_{26}H_{19}NO_5Cr$: C, 65.41; H, 4.01; N, 2.93. Found: C, 65.10; H, 4.10; N, 3.09.

Complex 3j: Yellow solid, mp 115 °C. IR: 2035 (m), 1970 (sh), 1915 (s) cm^{-1}. ^1H NMR: δ 4.20 (d, J = 14.6 Hz, 1H), 4.52 (d, J = 14.6 Hz, 1H), 5.33 (d, J = 14.6 Hz, 1H), 6.10 (d, J = 14.6 Hz, 1H), 6.80−7.02 (m, 2H), 7.08 (d, J = 7.3 Hz, 1H), 7.20−7.64 (m, 11H), 7.70 (d, J = 7.3 Hz, 2H), 7.88 (dd, J = 0.9 and 7.3 Hz, 1H). ^{13}C NMR: δ 58.01, 63.98, 116.87, 124.69, 125.11, 125.31, 126.66, 126.79, 127.78, 128.48, 129.05, 129.22, 129.47, 133.77, 134.13, 149.14, 217.06, 223.89, 281.34. Anal. Calcd for $C_{30}H_{21}NO_5Cr$: C, 68.18; H, 3.97; N, 2.84. Found: C, 67.96; H, 3.91; N, 2.75.

Complex 3k: Yellow solid, mp 111 °C. IR: 2070 (m), 1975 (sh), 1915 (s) cm^{-1}. ^1H NMR: δ 3.95 (s, 3H), 4.82 (d, J = 14.6 Hz, 1H), 4.70 (d, J = 14.6 Hz, 1H), 5.13 (d, J = 14.6 Hz, 1H), 5.82 (d, J = 14.6 Hz, 1H), 6.89−7.13 (m, 5H), 7.14−7.27 (m, 1H), 7.32−7.63 (m, 8H). ^{13}C NMR: δ 55.17, 56.31, 65.27, 110.94, 120.70, 121.86, 127.74, 127.82, 128.14, 128.54, 129.19, 134.03, 134.18, 141.56, 148.74, 198.47, 204.14, 258.97. Anal. Calcd for $C_{27}H_{21}NO_6W$: C, 63.91; H, 4.17; N, 2.76. Found: C, 64.07; H, 4.31; N, 2.47.

Complex 3l: Yellow solid, mp 146 °C. IR: 2050 (m), 1975 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 2.35 (s, 3H), 4.49 (s, 2H), 5.48 (s, 2H), 6.72−6.80 (m, 2H), 6.93−7.08 (m, 3H), 7.22−7.58 (m, 9H). ^{13}C NMR: δ 21.91, 56.36, 65.41, 116.78, 124.38, 127.34, 127.48, 127.81, 128.58, 128.91, 129.46, 134.23, 138.51, 153.25, 198.49, 204.22, 262.66. Anal. Calcd for $C_{27}H_{21}NO_5W$: C, 52.00; H, 3.37; N, 2.25. Found: C, 52.39; H, 3.27; N, 2.17.

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