along the ^1H frequency axis ω_2 (Figure 1b). The intensity of the individual fine structure components varies as cos $(\pi^3 J_{HN\alpha}\tau_2)$ and vanishes for $\tau_2^0 = 1/2^3 J_{HN\alpha}$ (Figure 1b,c). In practice, the experiment of Figure 1a is recorded repeatedly with different mixing periods τ_2. Upper and lower bounds on the range of values for the individual coupling constants $^3J_{HN\alpha}$ are determined by the longest τ_2 value for which the antiphase components of the ^{15}N-^1H cross peak conserve the initial signs, and the shortest τ_2 value for which the signs are inverted (Figure 1b).

With uniformly ^{15}N labeled 434 repressor (1-69), a DNA-binding protein consisting of 69 amino acid residues,[15] nine experiments with delays τ_2 of 52, 60, 68, 74, 80, 90, 100, 116, and 134 ms, respectively, were recorded. The spectral region shown in Figure 2 contains cross peaks between ^{15}N and ^{15}N-bound amide protons. The variation of the cross-peak intensities with τ_2 can readily be followed. For example, the cross peak corresponding to Ser 64 is not inverted up to a mixing time of 68 ms, disappears in the spectrum with τ_2 = 74 ms, and is inverted in the spectra with longer mixing times. Similarly, Leu 13 is inverted between 68 and 90 ms, and Arg 41 between 52 and 68 ms. Val 6 and Gln 17 conserve the sign of their cross-peak components unchanged up to 100 ms and vanish at 116 ms, whereas Asp 57 and Gln 22 conserve the same sign in all the spectra displayed, which corresponds to $^3J_{HN\alpha} < 4.3$ Hz. For comparison: in a 2QF-COSY spectrum recorded under the same conditions, no $^3J_{HN\alpha}$ value smaller than 6.5 Hz could be measured in this protein. The complete set of coupling constants $^3J_{HN\alpha}$ in the 434 repressor(1-69) measured with this method was found to coincide closely with the $^3J_{HN\alpha}$ values expected from the crystal structure of the 434 repressor(1-69)[16] (these data will be further discussed elsewhere).

With a small series of about three to four measurements with suitably selected τ_2 values, the experiment of Figure 1a can be used to determine whether a given $^3J_{HN\alpha}$ coupling constant falls into the range typical for α-helices ($^3J_{HN\alpha} < 6.0$ Hz), β-sheets ($^3J_{HN\alpha} > 8.0$ Hz), or conformationally averaged structure (6.0 Hz $\leq {}^3J_{HN\alpha} \leq$ 8.0 Hz).[8] This is usually sufficient for the preparation of the input for a high-quality protein-structure determination.[3-6] For more precise measurements of $^3J_{HN\alpha}$, two additional factors must be considered. First, one would have to account for the fact that other coherences besides $2H_y^N N_z$ are present at the outset of the τ_2 period (Figure 1a). These come from the evolution of the amide proton magnetization under $^3J_{HN\alpha}$ during the short delay τ_1. It can be shown that these additional terms cause a systematic increase of the measured, apparent $^3J_{HN\alpha}$ values by about 6% over the actual values of $^3J_{HN\alpha}$. Second, spin relaxation must be taken into account. With the inclusion of these two factors, the time course between the individual data points recorded at different τ_2 values could be fitted with an analytical function. This interpolation would allow the precise determination of τ_2^0 also between the discrete τ_2 values measured. In addition, the fit could be used to extrapolate experimental measurements at short τ_2 values to longer times, to determine the τ_2^0 values corresponding to small coupling constants $^3J_{HN\alpha}$ (Figure 1d). For small coupling constants, the main limitation of the experiment of Figure 1a results from the long delays τ_2 needed (Figure 1d), since spin relaxation will then greatly reduce its sensitivity.

The experimental scheme of Figure 1a can be extended by insertion of a $\pi(^{15}N)$ pulse at a time $\tau_1/2$ after the end of the evolution period t_1. This additional pulse refocuses the heteronuclear antiphase magnetization, so that ^{15}N broadband decoupling can be applied during the acquisition time t_2. In this version of the experiment, the phase ϕ_4 of the last $(\pi/2)(^1H)$ pulse must be along the x axis rather than along the y axis (see Figure 1a). Compared to the experiment of Figure 1a, the ^{15}N-decoupled spectrum can yield improvements in both sensitivity and resolution.

In a three-dimensional implementation of the experiment in Figure 1a, i.e., 3D J-resolved [^{15}N,^1H]-COSY, the delay τ_2 would be systematically incremented independently of the evolution period t_1 and a Fourier transformation along τ_2 would yield a third frequency dimension. The resulting spectrum consists of several [^{15}N,^1H]-COSY planes, with the peaks spread in the third dimension by $^3J_{HN\alpha}$. The multiplets along the $^3J_{HN\alpha}$ dimension have pure absorptive line shapes. For incompletely resolved multiplets, one would therefore encounter difficulties in a quantitative evaluation of $^3J_{HN\alpha}$ similar to those in a conventional one-dimensional ^1H NMR spectrum, or a homonuclear J-resolved 2D ^1H NMR spectrum.[18] In practice it appears preferable to measure the τ_2 dependence in the time domain by recording multiple heteronuclear 2D NMR spectra (Figure 2) than to extract the information on $^3J_{HN\alpha}$ from a line-shape analysis in the 3D NMR spectrum.[9d]

(15) (a) Anderson, J.; Ptashne, M.; Harrison, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *181*, 1307-1311. (b) Neri, D.; Szyperski, T.; Otting, G.; Senn, H.; Wüthrich, K. *Biochemistry* **1989**, *28*, 7510-7516. (c) Wider, G.; Neri, D.; Otting, G.; Wüthrich, K. *J. Magn. Reson.* **1989**, *85*, 426-431.

(16) Mondragon, A.; Subbiah, S.; Almo, S. C.; Drottar, M.; Harrison, S. C. *J. Mol. Biol.* **1989**, *205*, 189-201.

(17) De Marco, A.; Wüthrich, K. *J. Magn. Reson.* **1976**, *24*, 201-204.

(18) Nagayama, K.; Wüthrich, K. *Eur. J. Biochem.* **1981**, *115*, 653-657.

(19) Guëron, M.; Leroy, J. L.; Griffey, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7262-7266.

Stereochemistry of Nucleophilic Conjugate Addition. Addition of Ethanol-*d* and 2-Methyl-2-propanethiol-*d* to Ethyl Crotonate[1]

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As part of our effort toward a comprehensive understanding of the stereochemistry of addition and elimination reactions involving conjugated carbonyl compounds, we report that the base-catalyzed additions of ethanol-*d* and 2-methyl-2-propanethiol-*d* to ethyl crotonate demonstrate a surprisingly high stereoselectivity. The $(2R^*,3R^*)/(2R^*,3S^*)$ diastereomeric ratio of the addition products is approximately 10:1. Our results indicate that these nucleophilic additions proceed in two steps and that it is the second step, the protonation of the enolate anion, that determines the stereoselectivity of the reaction.

Although 1,4-conjugate nucleophilic additions to unsaturated carbonyl compounds are among the important reactions in organic synthesis[3] and biochemistry,[4] little has been published about their innate stereochemistry with simple, acyclic molecules.[5-8] In the few reports involving acyclic activated alkenes, all done in organic

(1) Presented in part at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; paper ORGN 91.

(2) Simpson College, Indianola, IA 50125.

(3) (a) Oare, D. A.; Heathcock, C. H. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Interscience: New York, 1989; Vol. 19, pp 227-407. (b) Duval, D.; Gëribaldi, S. In *The Chemistry of Enones, Part 1*; Patai, S., Rappoport, Z., Eds.; Interscience: New York, 1989; pp 355-469.

(4) Talalay, P.; De Long, M. J.; Prochaska, H. J. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 8261-8265.

(5) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 664-666. (b) Patai, S.; Rappoport, Z. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: New York, 1964; pp 491-501.

(6) (a) Bernhard, W.; Fleming, I.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1984**, 28-29. (b) Fleming, I.; Lewis, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 149-151. (c) Fleming, I.; Hill, J. H. M.; Parker, D.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1985**, 318-321. (d) Yamamoto, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1984**, 904-905. (e) Kawasaki, H.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1985**, *26*, 3031-3034. (f) Takaki, K.; Maeda, T.; Ishikawa, M. *J. Org. Chem.* **1989**, *54*, 58-62.

(7) Heathcock, C. H.; Henderson, M. A.; Oare, D. A.; Sanner, M. A. *J. Org. Chem.* **1985**, *50*, 3019-3022.

(8) Marchese, G.; Naso, F.; Schenetti, L.; Sciacovelli, O. *Chim. Ind. (Milan)* **1971**, *53*, 843-845.

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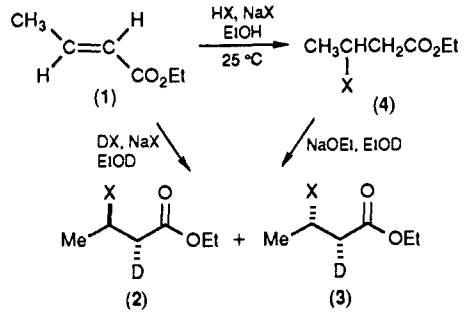
solvents of low polarity or with lithium enolates, ion pairing undoubtedly plays a role.[9] A few cyclic examples have also been published.[10-12] Given the great importance of conformational effects in the reactions of cyclic substrates, it is difficult to use them to understand stereoelectronic effects in addition and elimination reactions of conformationally mobile acyclic molecules.[13]

The addition of ethanol-*d* to ethyl crotonate (**1**) produced **2a** and **3a**. The reactions were carried out under N_2 using 0.010 M NaOEt and 0.46 M **1** (>99.9%) in EtOD (>99.5 atom % D). After the appropriate time (15 min-24 h), the reaction was neutralized with the necessary volume of 0.76 M D_2SO_4 and chromatographed on a short column of silicic acid. Quenching reactions with D_2SO_4 or H_2SO_4 gave the same stereochemical results. Proton NMR analysis of the nondeuterated ethyl 3-ethoxybutanoate (**4a**) in C_6D_6 showed peaks at δ 0.9-1.1 (m, 9 H), 2.2 (q, 1 H), 2.5 (q, 1 H), 3.3 (m, 2 H), 3.8 (m, 1 H), and 4.0 (q, 2 H). For determination of the reaction stereochemistry, multiple ^1H and ^2H NMR integrations were performed.



a, X = EtO; **b**, X = Me_3CS

The addition of EtOD across the C=C of **1** also produces products dideuterated at C-2. In addition, **1** undergoes H-D exchange at C-2 and C-4. In order to avoid these complications, the reaction was run to only 3% completion before ^1H and ^2H NMR analysis. Under these conditions, the percentages of **2a** and **3a** were 93% and 7%. This was shown most clearly by 46-MHz ^2H NMR spectroscopy, where the C-2 diastereotopic protons are at δ 2.42 and 2.15. Higher conversion percentages produced somewhat lower stereoselectivities due to the addition of EtOH to **1** which had earlier undergone H-D exchange, as well as possible dideuteration; at approximately 7% conversion, the product was 89% **2a** and 11% **3a**.

Determination of the configuration of **2a** was made possible by the availability of 3-hydroxy(2-$^2H_1$)butanoate of known 2*R**,3*R** relative configuration.[14] This was converted into **2a** by reaction of its alkoxide salt with ethyl iodide in 1,3-dimethyl-2-oxohexahydropyrimidine (DMPU). As in all of our other NMR spectra of 3-hydroxybutanoate derivatives, **2** had the C-2 proton in the downfield portion of the AB pattern and the C-2 deuteron upfield.[15]

One possible explanation for the high stereoselectivity could be the intervention of ion pairing, where a sodium ion bridges the heteroatoms of the addend and the enolate oxygen atoms and, thus, might hinder access of the electrophile from one side. However, the presence of crown ethers and changes in the metal cation had virtually no effect on the reaction stereochemistry. A concentration of 18-crown-6 2.5 times that of KOEt (0.01 M), which is large enough to complex almost all of the K^+,[16] gave 90% of the 2*R**,3*R** diastereomer as compared to 92% in the absence of crown ether. The presence of 15-crown-5 and 18-crown-6 at 14 times the concentration of sodium ethoxide in EtOD, and an increase of NaOEt by 50-fold, also gave little change. Use of lithium ethoxide at 0.05 M again gave no appreciable change in the stereochemistry. With these results, it is difficult to believe that ion pairing plays any major role in guiding the high stereoselectivity that we have observed.

The hypothesis that this high acyclic stereoselection results from a preferred geometry for reaction of the electrophile with the enolate anion was tested by studying the stereochemistry of nucleophilic addition to ethyl (*Z*)-2-butenoate. Unfortunately, in the presence of NaOEt/EtOD, the (*Z*)-alkene isomerizes to the *E* isomer with accompanying H-D exchange so quickly that analysis of the addition stereochemistry is impossible. We then turned to a sulfur nucleophile in the hope that nucleophilic addition would be faster than base-catalyzed isomerization of the (*Z*)-alkene. This was indeed the case.

Addition reactions of 2-methyl-2-propanethiol-*d* were carried out with 0.19 M Me_3CSD, Me_3CSNa, and **1** in EtOD at room temperature. Under these conditions, 89% **2b** and 11% **3b** were obtained, varying <0.5% in five reaction mixtures taken from 15-90% completion. The presence of Galvinoxyl did not change the diastereomeric product ratio. Reaction of ethyl (*Z*)-2-butenoate[17] under the same conditions gave 83% **2b** and 17% **3b**, with <1.5% variation in experiments from 6-70% completion. There was <4% isomerization of (*Z*)- to (*E*)-alkene at 70% completion. Only if the stereoselectivity is determined by the protonation of an enolate-anion intermediate, which has relatively free rotation about the C_2-C_3 bond, can addition of Me_3CSD to the two alkenes produce stereoconvergence. However, we are convinced that the small difference between 89% and 83% **2b** is real; it may indicate that the rate of protonation of the enolate competes with bond rotation or that a small amount of concerted addition of largely anti stereochemistry occurs.

The configurations of **2b** and **3b** were determined by NMR analyses. Base-catalyzed addition of Me_3CSH to ethyl 2-butynoate gave a mixture of ethyl (*E*)- and (*Z*)-3-(*tert*-butylthio)-2-butenoate,[18] which were separated by silica gel chromatography. Only the isomer given the *Z* configuration showed a large positive NOE between the allyl and vinyl protons. The (*E*)-alkene was deuterogenated in C_6H_6 in the presence of Wilkinson's catalyst, giving the 2*R**,3*S** diastereomer of ethyl 3-(*tert*-butylthio)(2,3-$^2H_2$)butanoate, which had its C-2 proton at δ 2.45.[15] The C-2 proton of **2b** was at δ 2.60.

To further demonstrate that the reaction stereoselectivity results from the protonation of the enolate, we studied the H-D exchange of **4**. Reaction of **4a** with 0.01 M NaOEt/EtOD gave 89% **2a** at approximately 7% conversion. Exchange of **4b** under identical conditions gave 87% **2b** at 11% conversion. Both of these results are virtually the same as those from the respective addition reactions.

This innate reaction stereoselectivity must come about through the influence of the C-3 chiral center on the protonation of the enolate anion. It could result from a steric effect, from a stabilizing influence of the ethoxy and *tert*-butylthio groups upon the antiperiplanar transition state, or from a combination of them.[6b,c,10,19-22] Our results from H-D exchange reactions of carbon and heteroatom β-substituted butanoate esters suggest that

(9) (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624-1654. (b) Arnett, E. M.; Harrelson, J. A., Jr. *Gazz. Chim. Ital.* **1987**, *117*, 237-243.
(10) Zimmerman, H. E. *Acc. Chem. Res.* **1987**, *20*, 263-268.
(11) (a) Hart, H.; Dunkelblum, E. *J. Am. Chem. Soc.* **1978**, *100*, 5141-5147. (b) Hart, H.; Chen, B.; Jeffares, M. *J. Org. Chem.* **1979**, *44*, 2722-2726.
(12) Kirby, A. J.; Logan, C. J. *J. Chem. Soc., Perkin Trans. 2* **1978**, 642-648.
(13) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973 and references therein.
(14) Mohrig, J. R.; Vreede, P. J.; Schultz, S. C.; Fierke, C. A. *J. Org. Chem.* **1981**, *46*, 4655-4658.
(15) Mohrig, J. R.; Dabora, S. L.; Foster, T. F.; Schultz, S. C. *J. Org. Chem.* **1984**, *49*, 5179-5182.
(16) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. I. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; pp 145-217.
(17) Taschner, M. J.; Rosen, T.; Heathcock, C. H. In *Organic Syntheses*; Kende, A. S., Ed.; Wiley: New York, 1986; Vol. 64, pp 108-113.
(18) Truce, W. E.; Tichenor, G. J. *J. Org. Chem.* **1972**, *37*, 2391-2396.
(19) Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845-2848.
(20) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108-1117.
(21) McGarvey, G. L.; Williams, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1435-1437.
(22) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353-3361.

stereoelectronic effects may be particularly important.[23]

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(23) Mohrig, J. R.; Franklin, S. J.; Larson, C. J.; Hirose, C. B.; Frisbie, C. D.; Warnet, R., submitted for publication in *J. Am. Chem. Soc.*

Addition of Methylene Chloride and Methyl Iodide to the Phenyl Ring of Aryl Imido/Amido Complexes of Rhodium[1]

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Growing interest in late-transition-metal oxo, imido, amido, alkoxo, and aryloxo complexes has resulted in the preparation of a number of complexes in which these ligands are highly basic.[2-4] The resulting reaction chemistry is dominated by the nucleophilic or basic properties of the heteroatom center. In this communication we report a novel and unusual reaction of a late-transition-metal aryl imido/amido complex which indicates that the high electron density at the nitrogen center has been distributed out into the aryl ring, inducing high nucleophilic reactivity at the para ring position.

Standing tautomeric mixtures of $Rh_2(\mu\text{-}NR)(CO)_2(\mu\text{-dppm})_2$ and $Rh_2(\mu\text{-}NHR)(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ (**1/2**) [R = *p*-MeC_6H_4, dppm = bis(diphenylphosphino)methane, dppm-H = bis(diphenylphosphino)methanide][1,2b] in CH_2Cl_2 leads to a slow reaction yielding a new product formulated as $[Rh_2(\mu\text{-}NC_6H_4Me(CH_2Cl))(CO)_2(\mu\text{-dppm})_2]^+Cl^-$ (**3**) (eq 1).[5] The re-

$$\mathbf{1/2}\ (R = p\text{-}MeC_6H_4) + CH_2Cl_2 \rightarrow [Rh_2(\mu\text{-}NC_6H_4Me(CH_2Cl))(CO)_2(\mu\text{-dppm})_2]^+Cl^- \quad (1)$$

action takes several days to reach ca. 90% completion and involves an unusual formal addition of CH_2Cl^+ to the para position of the imido/amido ring of **1/2** (R = *p*-MeC_6H_4).

The ^1H NMR spectrum of **3** is quite distinctive with a clear A_2B_2 pattern for the former aryl ring upfield of the aromatic region. An upfield shift is also observed for the ring methyl group, indicating a loss of aromaticity in the ring. The ^{31}P NMR spectra of **3** are symmetric and suggest dynamic exchange[6] or undetectable differences in the phosphorus atom environments.

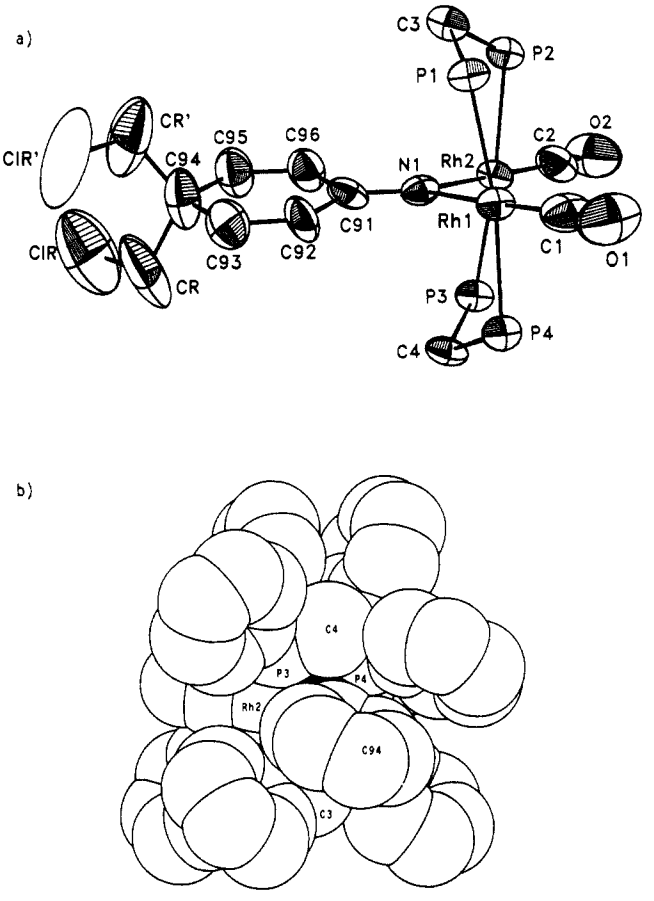

Figure 1. Drawings of the cationic portion of **3**, $[Rh_2(\mu\text{-}NC_6H_4Me(CH_2Cl))(CO)_2(\mu\text{-dppm})_2]^+Cl^-$. (a) ORTEP, 50% probability ellipsoids. Phenyl rings omitted. The open ellipsoid of ClR′ represents the minor position for the CH_2Cl group (see text). Selected bond distances (Å): Rh1-N, 2.05 (1); Rh2-N, 2.04 (1); N1-C91, 1.29 (2); C91-C92, 1.46 (2); C91-C96, 1.48 (2); C92-C93, 1.31 (2); C96-C95, 1.32 (2); C93-C94, 1.48 (2); C95-C94, 1.52 (3); C94-CR, 1.58 (3); C94-CR′, 1.50 (3); CR-ClR, 1.67 (2); CR′-ClR′, 1.48 (4). Selected bond angles (deg): Rh1-N-Rh2, 97.3 (4); Rh1-N-C91, 129.1 (9); Rh2-N-C91, 133.5 (9); N1-C91-C92, 123 (1); N1-C91-C96, 122 (1); C92-C91-C96, 115 (1); C91-C92-C93, 121 (1); C91-C96-C95, 122 (1); C92-C93-C94, 127 (2); C96-C95-C94, 125 (1); C93-C94-C95, 109 (1); C93-C94-CR, 105 (2); C93-C94-CR′, 109 (2); C95-C94-CR, 105 (2); C95-C94-CR′, 111 (2); CR-C94-CR′, 117 (2); C94-CR-ClR, 112 (2); C94-CR′-ClR′, 116 (2). (b) PLUTO, van der Waals radii. Substituents CR, CR′, Cl, and Cl′ omitted from C94. Darkened area is N1.

An ORTEP diagram of the cationic portion of **3** is shown in Figure 1a.[7] The ring methyl group and the CH_2Cl group are disordered. This results in full occupancy of both carbon atom positions CR and CR′ but only partial occupancy of the chlorine atom positions. Occupancy refinement of ClR and ClR′ suggests a 35% and 65% distribution with ClR being the major position. An inspection of the N-C and C-C distances and angles (figure caption) clearly shows the quinoid-like structure represented in I.

As expected from the above results, methyl iodide also adds to the aryl ring of **1/2** (R = *p*-MeC_6H_4). The reaction is complete within minutes, and the only detectable product is $[Rh_2(\mu$-

(1) Late Transition Metal μ-Oxo and μ-Imido Complexes. 5. For part 4, see: Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632-2640.

(2) (a) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234-2236. (b) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. (c) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231-3234.

(3) (a) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543-8545. (b) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719-2721.

(4) (a) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163-1188. (c) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1-40. (d) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750-4761. (e) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563-6565.

(5) Data for $[Rh_2(\mu\text{-}NC_6H_4Me(CH_2Cl))(CO)_2(\mu\text{-dppm})_2]^+Cl^-$ (**3**): IR (CH_2Cl_2) 1990 (m), 1975 cm^{-1} (s); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.1-7.7 (m, 40 H, Ph), 5.73 and 5.53 (2 d, J_{HH} = 10 Hz, 2 × 2 H, C_6H_4), 3.41 (s, 2 H, CH_2Cl), 3.22 and 3.06 (2 m, 2 × 2 H, PCH_2P), 1.09 (s, 3 H, CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 22.8 (dm, J_{RhP} = 136.6 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 52.0 (s, CH_2Cl), 25.0 (s, CH_3), 21.3 (m, PCH_2P).

(6) The NMR spectra (^1H and ^{31}P) do show some broadening at -80 °C.

(7) Crystal data for **3**, $C_{60}H_{53}Cl_2NO_2P_4Rh_2 \cdot CH_2Cl_2$ (fw = 1306.64): monoclinic (*C*2/*c*), *a* = 37.20 (1) Å, *b* = 12.827 (3) Å, *c* = 26.497 (6) Å, β = 97.35 (2)°, *V* = 12538 Å^3, d_{calcd} = 1.38, *Z* = 8. Data (Mo Kα) were collected on a CAD4 diffractometer. The structure was solved by Patterson methods (SHELXS-86; Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Godard R., Eds.; Oxford University Press: London, 1985; pp 175-189) and refined by full matrix least squares refinement (SDP) to R = 0.065 and R_w = 0.087 for 3858 absorption-corrected observations with $F_o^2 > 2\sigma(R_o^2)$ and 673 variables. Details will be provided in a forthcoming full paper.

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