

## A Nondegradative Reaction of Active Nitrogen. Conversion of Ethanol to Acetamide

Sir:

We have previously reported<sup>1</sup> the interception of HCN precursor(s) in the reaction of active nitrogen with methanol in aqueous solution. In this work it was shown that tetranitromethane suppresses formation of HCN from methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol. In the case of methanol, the decrease in yield of HCN associated with the presence of tetranitromethane is accompanied by an equimolar increase in the yield of ethylene glycol. No carbonaceous nitrogenous product other than HCN was found in the previous work with methanol. We now find that the major nitrogenous product of the reaction of aqueous active nitrogen with ethanol is acetamide. *This appears to be the first reported case of efficient nondegradative incorporation of nitrogen into an organic molecule resulting from reaction with active nitrogen.*<sup>2</sup> Smaller yields of amides have also been obtained from methanol and isopropyl alcohol.

Experimental procedures were the same as those which were reported previously.<sup>1</sup> Acetamide was isolated by evaporating the combined solutions from four 20-min runs employing 5 M ethanol, first in a rotary evaporator under reduced pressure at 31–35° and then to dryness over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator. The solid product was recrystallized once from HCCl<sub>3</sub>-*n*-hexane and identified as acetamide by the absence of any depression in its mixture melting point with an authentic sample and by the identity of its infrared spectrum in chloroform solution with that of the authentic material. Quantitative yields of acetamide were determined by the method of Robertson, *et al.*,<sup>3</sup> which involves formation of the hydroxamic acid at steam-bath temperature and measurement of optical absorption due to the Fe<sup>III</sup> complex of the latter. This method does not distinguish between acetamide and ethyl acetate. Ethyl acetate would have been removed during the isolation and recrystallization of acetamide. It was therefore shown that reacted solutions respond to the method of Goldenberg<sup>4</sup> in exactly the same way as does acetamide and are substantially less reactive than ethyl acetate. In this method, the hydroxamic acid is generated at room temperature and is formed much more slowly by amides than by esters.

With an incident N(<sup>4</sup>S) flow rate<sup>5</sup> of 50 × 10<sup>-8</sup> mol sec<sup>-1</sup>, product yields from the reaction of 1–10 M aqueous solutions of ethanol for 5 min were (in units of 10<sup>-8</sup> mol sec<sup>-1</sup>): HCN,<sup>6</sup> 19; CH<sub>3</sub>CONH<sub>2</sub>,<sup>3</sup> 29; NH<sub>3</sub>,<sup>7</sup> 3; NH<sub>2</sub>NH<sub>2</sub>,<sup>8</sup> <0.1; CH<sub>3</sub>CHO,<sup>9</sup> 6.5. Thus, about 60% of incident N(<sup>4</sup>S) is fixed as acetamide

(1) C. T. Chen and N. N. Lichtin, *J. Amer. Chem. Soc.*, **92**, 7506 (1970).

(2) In the gas phase the reaction of ethanol with active nitrogen gives HCN, H<sub>2</sub>O, and H<sub>2</sub> as the main products along with small amounts of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CH<sub>3</sub>CN, C<sub>2</sub>N<sub>2</sub>, CO, and CH<sub>3</sub>CHO. See P. A. Gartaganis, *Can. J. Chem.*, **43**, 935 (1965).

(3) E. B. Robertson, B. D. Sykes, and H. B. Dunford, *Anal. Biochem.*, **9**, 158 (1964).

(4) V. Goldenberg, *Anal. Chem.*, **30**, 1327 (1958).

(5) Determined by NO titration.

(6) J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).

(7) A. Matsumoto, N. Hayashi, and N. N. Lichtin, *Radiat. Res.*, **41**, 299 (1970).

(8) G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

(9) E. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).

while most of the balance appears in HCN. Reaction of 1–5 M aqueous ethanol saturated with tetranitromethane (1.0–1.5 × 10<sup>-2</sup> M) with 50 × 10<sup>-8</sup> mol sec<sup>-1</sup> of active nitrogen for 5 min gave no detectable HCN,<sup>6</sup> *i.e.*, less than 0.2 × 10<sup>-8</sup> mol sec<sup>-1</sup>. Other yields (in units of 10<sup>-8</sup> mol sec<sup>-1</sup>) were: "CH<sub>3</sub>CONH<sub>2</sub>,"<sup>3</sup> 7 (sum of amide and ethyl acetate); NH<sub>3</sub>,<sup>7</sup> 1; CH<sub>3</sub>CHO,<sup>9</sup> 44; HC(NO<sub>2</sub>)<sub>3</sub>,<sup>10</sup> 19. Under identical conditions, except that the discharge was not running, the yields of "CH<sub>3</sub>CONH<sub>2</sub>," CH<sub>3</sub>CHO, and HC(NO<sub>2</sub>)<sub>3</sub> from 5 M EtOH were 5, 7, and 0.7, respectively. The data obtained in the presence of TNM can be interpreted as indicating that precursors of HCN and acetamide are intercepted by tetranitromethane. It is proposed that a key precursor of both these products is the CH<sub>3</sub>CH(OH)NH radical.

The generality of such nondegradative incorporation of nitrogen into organic molecules is under investigation. Preliminary data indicate that little nitrogen, no more than 2%, is fixed as formamide<sup>3</sup> in the reaction of CH<sub>3</sub>OH with active nitrogen. However, with isopropyl alcohol ~30% of incident N is fixed as amide nitrogen,<sup>3</sup> presumably in acetamide and/or *N*-methylacetamide.

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(10) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **71**, 4544 (1967).

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## Carbon-13 Nuclear Magnetic Resonance of Some Group VIb Metal Carbonyls and Derivatives<sup>1</sup>

Sir:

While application of carbon-13 nuclear magnetic resonance (cmr) to problems of organic chemistry is now becoming routine, few spectra of metal carbonyls or organotransition metal complexes have been reported.<sup>2–5</sup> Considering the current interest in cmr, studies to determine factors which influence carbonyl chemical shifts are needed, especially in view of contention in the literature with regard to the use of carbonyl stretching frequencies, force constants and band intensities,<sup>6</sup> and proton<sup>5</sup> and <sup>31</sup>P coupling constants and chemical shifts<sup>6–8</sup> in efforts to assess inductive (σ) and mesomeric (π) effects of a ligand (L) on metal-carbonyl bonding. Accordingly, cmr spectra of the three group VIb metal carbonyls M(CO)<sub>6</sub> (M = Cr,

(1) Presented in part at the 3rd *Inorganica Chimica Acta* Symposium, Venice, Italy, Sept 1970, and the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) O. A. Gansow and B. Y. Kimura, *Chem. Commun.*, 1621 (1970).

(3) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); *J. Chem. Soc. A*, 861 (1967).

(4) H. L. Retkofsky, E. N. Frankel, and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **88**, 2710 (1966).

(5) P. C. Lauterbur and R. B. King, *ibid.*, **87**, 3266 (1965).

(6) For a recent succinct review containing appropriate references, see S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).

(7) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970); R. T. Bertrand, F. C. Ogilvie, and J. G. Verkade, *ibid.*, **92**, 1908 (1970); R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969), and references cited therein.

(8) G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).

**Table I.**  $^{13}\text{C}$  Nmr Data for Group VIb Metal Carbonyls and Derivatives

Ligand-metal	$\delta(^{13}\text{C}),^a$	$\delta(^{13}\text{C}),$	$k_1(\text{t})$	$k_2(\text{c})$	$^1J(^{183}\text{W}^{13}\text{C}),$		$^2J(^{31}\text{P}^{13}\text{C}),$	
	cis <sup>b</sup>	trans			cis	$^1J(^{183}\text{W}^{31}\text{P})$	cis	trans
$(\text{C}_6\text{H}_5\text{O})_3\text{P}-\text{W}$	194.5	197.0	15.88	16.08		411	10.5	45.4
$(n\text{-C}_4\text{H}_9\text{O})_3\text{P}-\text{W}$	196.1	198.8	15.79	15.90		390	9	36
$(\text{C}_6\text{H}_5)(n\text{-C}_4\text{H}_9\text{O})_2\text{P}-\text{W}$	196.9	200.0	15.75	15.91			9	29
$(\text{C}_6\text{H}_5)_2(n\text{-C}_4\text{H}_9\text{O})\text{P}-\text{W}$	197.5	199.0	15.69	15.87			9	27
$(\text{C}_6\text{H}_5)_3\text{Sb}-\text{W}$	197.0	199.1	15.61	15.96	127			
$(\text{C}_6\text{H}_5)_3\text{As}-\text{W}$	197.5	199.7	15.53 <sub>5</sub>	15.90	124			
$(\text{C}_6\text{H}_5)_3\text{Bi}-\text{W}$	197.8	198.3	15.53 <sub>5</sub>	15.97	126			
$(\text{C}_6\text{H}_5)_3\text{P}-\text{W}$	198.0	199.8	15.52	15.88	129	280	7	22
$\text{C}_6\text{H}_{11}\text{NH}_2-\text{W}$	199.1	201.9	15.12	15.76	132			
$\text{CO}-\text{W}$	192.1			16.41	<i>c</i>			
$\text{CO}-\text{Mo}$	202.0			16.52				
$\text{CO}-\text{Cr}$	212.5			16.49				

<sup>a</sup>  $\pm 0.1$  ppm downfield from internal TMS. <sup>b</sup> Cis and trans refer to the relationship of the carbon and phosphorus atoms. <sup>c</sup>  $J(\text{W}-\text{C}) = 126$  Hz.

Mo, W) and monosubstituted complexes  $\text{LW}(\text{CO})_5$  [ $\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3, \text{P}(\text{O}-n\text{-C}_4\text{H}_9)_3, \text{P}(\text{O}-n\text{-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5), \text{P}(\text{O}-n\text{-C}_4\text{H}_9)(\text{C}_6\text{H}_5)_2, \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3, \text{Bi}(\text{C}_6\text{H}_5)_3, \text{NH}_2(\text{C}_6\text{H}_{11})$ ] have been obtained.

Time averaging, employing a Bruker HFX-10 spectrometer and *ca.* 0.5 *M* methylene chloride solutions of the natural isotopic abundance metal carbonyl or derivative,<sup>9</sup> afforded the spectra, for which chemical shift and coupling data are given in Table I.

Each substituted group VIb metal carbonyl yields two sets of signals, corresponding to resonances of the cis and trans carbonyls.<sup>2</sup> Phosphorus-containing ligands divide each carbon resonance into a doublet. Molecules containing  $^{31}\text{P}$ ,  $^{13}\text{C}$ , and  $^{183}\text{W}$  nuclei exhibit two sets of carbonyl resonances of relative intensities 4:1, each set consisting of a group of signals of intensity ratios 1:1:11.5:1:1, in accordance with the 14.4% natural abundance of the  $^{183}\text{W}$  isotope. With broadband proton decoupling, a single set of resonances may be assigned to each chemically unique ligand carbon.<sup>10</sup>

In the absence of large anisotropic effects, carbonyl cmr chemical shifts are dominated by the paramagnetic term of the Saika-Slichter screening equation.<sup>11</sup> Factors affecting this term, which are discussed in detail elsewhere,<sup>2, 12-14</sup> include the radius of the carbon 2p orbital (inverse relationship), the energy separation between the ground state and the lowest energy paramagnetic excited state (inverse relationship), and the extent of  $\pi$  bonding to carbon (direct relationship). The latter two factors are expected to result in increased paramagnetic shielding as the ability of the substituent L to  $\pi$  bond to the metal decreases,<sup>15</sup> while the first is expected to exert an opposing effect.<sup>16</sup>

(9) The  $^{183}\text{W}-^{13}\text{C}$  coupling constant for  $\text{W}(\text{CO})_5$  was obtained employing a sample of  $\text{W}(\text{CO})_5$  containing approximately 8 mol %  $^{13}\text{C}$ .

(10) Discussion of aromatic or alkyl chemical shifts or coupling constants is not given here. Reference 2 contains some preliminary comments.

(11) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(12) M. Karplus and J. A. Pople, *ibid.*, **32**, 2803 (1963).

(13) A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).

(14) J. A. Pople, *Mol. Phys.*, **7**, 310 (1964).

(15) The ultraviolet spectra for a series of  $\text{LCr}(\text{CO})_5$  complexes indicate that the energy of the first charge-transfer band decreases in energy with decreased ligand-to-Cr  $\pi$  bonding (and thus with increased Cr-C-O  $\pi$  bonding): P. S. Braterman and A. P. Walker, *Discuss. Faraday Soc.*, **No. 47**, 121 (1969).

(16) See, e.g., D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1286 (1968).

Changes in ligand-metal  $\pi$  bonding are generally conceded to dominate changes in carbonyl stretching frequencies and force constants in octahedral metal carbonyls and their substitution products.<sup>6</sup> Accordingly, Cotton-Kraihanzel carbonyl stretching force constants,  $k_1$  (axial carbonyl) and  $k_2$  (equatorial carbonyls),<sup>17</sup> have been plotted against the corresponding  $^{13}\text{C}$  chemical shifts as obtained in this investigation. The satisfactory linear relationship obtained (Figure 1) strongly suggests that for a given metal, changes in M-C-O  $\pi$

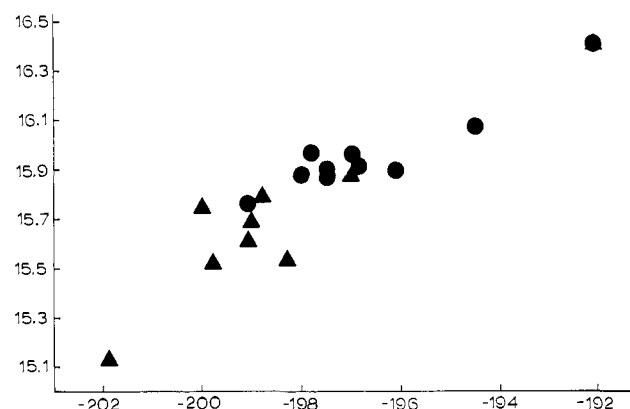


Figure 1. Plot of carbonyl stretching force constants *vs.* carbon-13 carbonyl chemical shifts for tungsten carbonyl complexes: ordinate  $k$ , m dyn/A; abscissa  $\delta$ , ppm downfield from TMS; ●, equatorial carbonyls; ▲, axial carbonyls.

bonding exert a dominant influence on  $^{13}\text{C}$  chemical shifts. These results are consistent with those obtained for a series of  $(\pi\text{-cyclopentadienyl})\text{Fe}(\text{CO})_2\text{X}$  complexes ( $\text{X} =$  one-electron-donating substituent), for which electron withdrawal by X from the metal effected *upfield*  $^{13}\text{C}$  chemical shifts,<sup>18</sup> since amines, phosphines, and phosphites are, relative to CO, electron-donating ligands.

It should be noted, however, that there are substantial shift differences among the three group VIb hexacarbonyls, while the carbonyl stretching force constants for these complexes differ little. Moreover, their ul-

(17) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

(18) O. A. Gansow and B. Y. Kimura, *ibid.*, submitted for publication.

traviolet spectra are also quite similar;<sup>19</sup> a plausible explanation for the observed differences is not evident at this time.

The several <sup>183</sup>W-<sup>13</sup>C coupling constants measured (Table I) are observed to vary little with the identity of the ligand, increasing by only 6 Hz from W(CO)<sub>6</sub> to (cyclohexylamine)W(CO)<sub>5</sub>. The parameters which can be considered to determine relative values of the metal-carbon coupling constants in a series of similar complexes are the M-C σ-bond order and the values of |Ψ<sub>c</sub>(0)|<sup>2</sup>, |Ψ<sub>m</sub>(0)|<sup>2</sup>.<sup>20</sup> Substitution of an amine for a CO would increase the value of |Ψ<sub>m</sub>(0)|<sup>2</sup> but weaken the W-C σ bonds.<sup>8</sup> Thus the two effects might largely balance one another, producing the observed small variations. It will be of interest to compare <sup>183</sup>W-<sup>31</sup>P and <sup>183</sup>W-<sup>13</sup>C coupling constants in a series of complexes; such a study, which requires <sup>13</sup>C enrichment of the LW(CO)<sub>5</sub> molecules, is presently in progress.

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(19) See, e.g., N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968). However, the observed shifts do exhibit a linear inverse relationship to the energy separations between the 2t<sub>1u</sub> and 4t<sub>1u</sub> molecular orbitals for this series of complexes.

(20) Any assumption that *J*(<sup>183</sup>W-<sup>13</sup>C) is dominated by the s character of the Fermi contact term must be considered tentative, since there is no evidence that the effective nuclear charge (*Z*\*), important for *J*(<sup>13</sup>C-<sup>1</sup>H), may not be equally important here: D. M. Grant and W. Lichtman, *ibid.*, **87**, 3994 (1965).

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## Structure of the Dimer of Niobocene

Sir:

Most of the parent bis (cyclopentadienyl) transition metal complexes studied have the familiar π-bonded "sandwich" structure. However, the bis(cyclopentadienyl) complexes of niobium, tantalum, and titanium have a more complex structure. Recently the bis(cyclopentadienyl)niobium complex was synthesized, and a novel dimeric structure was proposed to account for its nmr spectrum.<sup>1</sup> We report here the molecular and crystal structure of the dimeric bis(cyclopentadienyl)niobium complex, [(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>)NbH]<sub>2</sub>.

The preparation and spectral characterization of [(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>)NbH]<sub>2</sub> were reported earlier.<sup>1</sup> We obtained triclinic or orthorhombic crystals depending on the solution concentration. At certain dilute concentrations we got both modifications, which were morphologically separable. The cell size and crystal density of the triclinic form are consistent with two dimeric

(1) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

molecules, 2[(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>)NbH]<sub>2</sub>, and two benzene molecules per unit cell. The ir spectrum also showed the presence of benzene. The unsolvated orthorhombic crystals were used in this study.

Crystals of niobocene dimer, [(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>4</sub>)NbH]<sub>2</sub>, are brown, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with cell dimensions of *a* = 15.384 (4), *b* = 24.487 (5), and *c* = 12.879 (3) Å. The observed and calculated densities for 12 dimeric molecules per cell are 1.85 and 1.83 g/cm<sup>3</sup>, respectively. There are three crystallographically unique dimers per cell. Data were measured out to 2θ = 45° on a Picker four-circle automatic diffractometer using the θ-2θ scan technique and Mo Kα radiation. The crystal was enclosed in a capillary for protection, although crystals are not nearly as reactive as solutions. The data were corrected for absorption effects; the linear absorption coefficient is 13.69 cm<sup>-1</sup>. The niobium atoms were found using Patterson superposition techniques in conjunction with the minimum function. The remaining atoms were found on electron density difference maps. The structure was refined by least-squares to a current conventional *R* of 0.066 for the 2620 observed reflections. There was clear evidence in electron density difference maps for nearly all of the hydrogen atoms including two of the six unique hydride hydrogens.

The molecular structure is that of a dimeric metal hydride with a Nb-Nb bond, terminal hydride hydrogens and cyclopentadienyl groups, and bridging C<sub>5</sub>H<sub>4</sub> groups, as shown in Figure 1. The C<sub>5</sub> rings are bent back to an angle of 39.7 (9)° to accommodate the novel bridging structure. In this way, the metal atoms are able to achieve an inert gas electronic structure. The hydride hydrogen positions in Figure 1, located as the highest peaks in an electron density difference map, were not refined. Clearly they are in the stereochemically active site expected for the hydrogen atom. The only other examples of C<sub>5</sub>H<sub>4</sub> groups bridging metal atoms are in (C<sub>5</sub>H<sub>5</sub>)(CO)M(C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>4</sub> (M = Mo, W)<sup>2</sup>, (C<sub>5</sub>H<sub>5</sub>)(H)Re(C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>4</sub>,<sup>2</sup> and [(C<sub>5</sub>H<sub>5</sub>)Ti(C<sub>5</sub>H<sub>4</sub>)Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>.<sup>3</sup> The angles between the C<sub>5</sub>H<sub>5</sub> rings in the latter structures are 35° in (C<sub>5</sub>H<sub>5</sub>)(CO)Mo-(C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>4</sub> and 44° in [(C<sub>5</sub>H<sub>5</sub>)Ti(C<sub>5</sub>H<sub>4</sub>)Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>. This angle is 34 (1)° in the monomeric (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoH<sub>2</sub>.<sup>4</sup>

The crystal structure consists of the packing of discrete molecules such as that depicted in Figure 1. Of the three crystallographically unique dimers, two are like that shown and one is the other enantiomorph. The molecular structures are the same within experimental errors. Hence the molecular dimensions quoted here have been averaged over all chemically equivalent distances (angles) and the errors estimated according to

$$\left[ \sum_1^n (d_i - \bar{d})^2 / n(n-1) \right]^{1/2}$$

where *d<sub>i</sub>* and  $\bar{d}$  are the distances (angles) and mean distance (angle), respectively.

All of the C<sub>5</sub> rings are essentially planar with the maximum deviation being 0.02 Å. The average Nb-

(2) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *ibid.*, **93**, 536 (1971).

(3) The crystal structure of [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiAl(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> is reported: P. Corradini and A. Sirigu, *Inorg. Chem.*, **6**, 601 (1967). However, we believe this complex has *bona fide* C<sub>5</sub>H<sub>4</sub> bridging rings as also recognized by P. C. Waiiles and H. Weigold, *J. Organometal. Chem.*, **24**, 713 (1970).

(4) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).