

Evidence for Ambiphilic Behavior in $(\text{CO})_5\text{W}=\text{NPh}$. Conversion of Carbonyl Compounds to *N*-Phenyl Imines via Metathesis

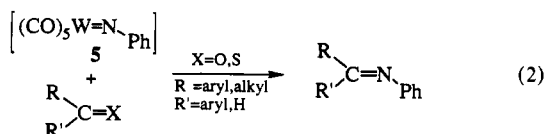
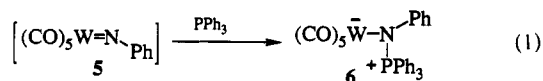
Bruce A. Arndtsen, Hanadi F. Sleiman, Andrew K. Chang, and Lisa McElwee-White*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305.
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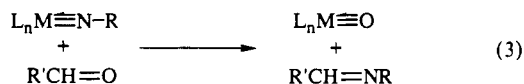
Abstract: $(\text{CO})_5\text{W}=\text{NPh}$ (**5**) has been generated in the presence of aldehydes, ketones, and thioketones and found to undergo metathesis with these substrates to yield *N*-phenyl imines. The participation of complex **5** as a nucleophile in these reactions and the previously reported reaction of **5** with PPh_3 confirm the ambiphilic nature of $(\text{CO})_5\text{W}=\text{NPh}$. This is consistent with the electronic structure of the model compound $(\text{CO})_5\text{W}=\text{NMe}$, as obtained from extended Hückel calculations. The heteroatom-substituted nitrene complex $(\text{CO})_5\text{W}=\text{NNMe}_2$ (**7**) is less electrophilic but still functions as a nucleophile in its reaction with PhCHO to give $\text{Me}_2\text{NN}=\text{CHPh}$.

Introduction

We recently reported¹ the isolation of a zwitterionic intermediate $(\text{CO})_5\text{WPhNPhC}(\text{OCH}_3)\text{CH}_3$ (**3**) from the metathesis reaction of $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{CH}_3$ (**1**) and photochemically generated *cis*-azobenzene (**2-C**). Zwitterion **3** was found to decompose photochemically or thermally via a unimolecular pathway² to yield imidate **4** and the transient low-valent nitrene complex $(\text{CO})_5\text{W}=\text{NPh}$ (**5**) (Scheme I). Electrophilic behavior of the nitrene complex **5** has been demonstrated through addition of the nucleophile PPh_3 to yield phosphine ylide (or phosphinimine complex) **6** (eq 1).² We now report that complex **5** also undergoes metathesis with electrophilic aldehydes, ketones, and thioketones to produce imines (eq 2).

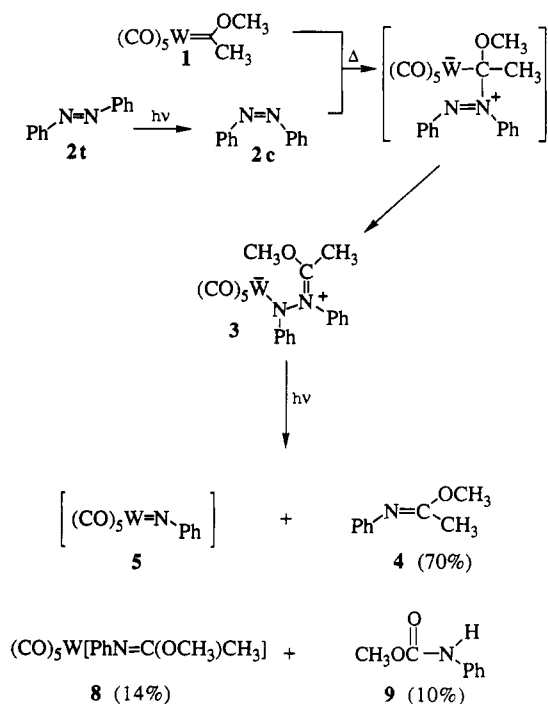


The vast majority of transition-metal nitrene, or imido, complexes are in high oxidation states, with linear and relatively stable metal-imido bonds.³ These complexes can exhibit either electrophilic or nucleophilic behavior at the imido nitrogen, depending upon the nature of the metal and ancillary ligands. Nucleophilic imido complexes commonly react with aldehydes to yield imines (eq 3).^{3c,4} For example, the diimido-chromium complex



$(\text{Me}_3\text{SiO})_2\text{Cr}(\text{N}^t\text{Bu})_2$ reacts with benzaldehyde to produce phenyl *tert*-butyl imine and the chromium oxo species.⁵ The replacement of an imido with an oxo ligand is thought to provide the ther-

Scheme I



modynamic driving force for these reactions.^{3c} While there are many examples of nucleophilic linear imido ligands, the bending of the imido ligand is believed to increase its nucleophilicity, as demonstrated by the protonation^{6a} or methylation^{6b} of the bent imido ligand of $(\text{S}_2\text{CNEt}_2)_2\text{Mo}(\text{NPh})_2$, while the linear ligand remains intact. The only isolated and characterized low-valent imido complex to date also shows nucleophilic behavior. This compound, $\text{Cp}^*\text{IrN}^t\text{Bu}$, reacts with MeI to produce $^t\text{BuNMe}_3\text{I}$ as well as undergoing cycloaddition with CO_2 to form a metal-lacycle.⁷

Electrophilic imido complexes, though less well-known, have also been prepared. Iron and manganese porphyrin-nitrene complexes are known to react electrophilically with olefins to produce aziridines.⁸ The chromium-diimido complex $(\text{Me}_3\text{SiO})_2\text{Cr}$ -

(1) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700-8701.

(2) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007-8009.

(3) For reviews of imido complexes, see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175. (b) Cenini, S.; LaMonica, G. *Inorg. Chim. Acta* **1976**, *18*, 279-293. (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(4) Examples: (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094-5095. (b) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7809-7811. (c) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077-3081.

(5) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965-969.

(6) (a) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. *D. Inorg. Chem.* **1980**, *19*, 1055-1059. (b) Maatta, E. A.; Wentworth, R. A. *D. Inorg. Chem.* **1979**, *18*, 2409-2413.

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(8) (a) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517-1524. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161-1163. (c) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073-2074.

(*N*'Bu)₂ yields *N*-*tert*-butylaniline upon reaction with Ph₂Zn, though the initial site of attack remains unclear.⁹ Recently, Brookhart and Templeton have reported the cationic tungsten-imido complexes, [Tp'(CO)₂WNR]I (R = *t*BuPh), which react as electrophiles with LiBH₄ to produce the amido complexes.¹⁰

In contrast to the high-valent imido compounds, zero-valent nitrenes of the form (CO)₅M=NR (M = Cr, W) have thus far eluded isolation, although species of this type have been invoked as reactive intermediates.^{1,2,11} and the amino-substituted nitrene, (CO)₅W=NNMe₂ (7), has recently been observed spectroscopically.¹² These complexes bear a striking resemblance to the Fischer carbenes (CO)₅W=CRR', which have been used in a wide variety of transformations involving transfer of the carbene fragment.¹³ This similarity suggests that low-valent nitrene complexes may provide interesting new routes to analogous products incorporating the nitrene moiety. To date, there have been very few reports on the reactivity of nitrene complexes of this type.^{2,11,12} The formation of phosphine ylide 6 from nitrene complex 5 was a confirmation that these species could exhibit reactivity comparable to their carbon analogues,² which are known to form similar adducts.¹⁴ However, reaction of 5 with aldehydes and ketones demonstrates that this complex can also function as a nucleophile and is indicative of novel ambiphilic behavior for a transition-metal nitrene compound.

Results and Discussion

Formation and Decomposition of Zwitterion 3. (CO)₅WPhNPhC(OCH₃)CH₃ (3) is formed immediately upon combination of *cis*-azobenzene (2-C) with tungsten carbene 1 in methylene chloride or benzene at room temperature. Evaporation of the solvent and washing the residue with pentane to remove unreacted starting material leaves 3 as a dark red oil in 75% yield. IR and multinuclear NMR spectroscopy have shown this product to have the zwitterionic structure shown in Scheme I.^{1,15}

Both thermal and photochemical decomposition of 3 yield the organic metathesis product PhN=C(OCH₃)CH₃ (4). The photochemical decomposition is much cleaner and produces the uncomplexed imide 4 in 70% yield. Also formed is the imide complex (CO)₅W[PhN=C(OCH₃)CH₃] (8) in 14% yield. The identification of 8 was confirmed upon preparation of an authentic sample by the photolysis of W(CO)₆ in the presence of imide 4. Complex 8 presumably arises in the reaction mixtures from the coordination of free imide to (CO)₅W fragments generated during the reaction.

A rather intriguing result of the decomposition of 3 is the formation of CH₃O(CO)NPh (9) in 10% yield.¹⁷ While the mechanism for the formation of this compound is not clear at this time, carbamate 9 is formally the product of the methanol trapping of phenyl isocyanate. However, neither phenyl isocyanate nor

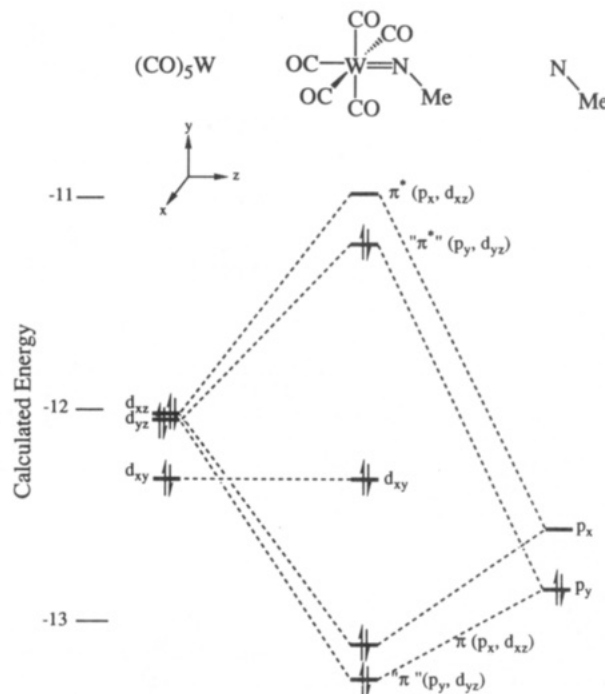


Figure 1. Orbital mixing diagram for the formation of 10 from the fragments (CO)₅W and NMe. Energy levels are from the extended Hückel calculations described in the text.

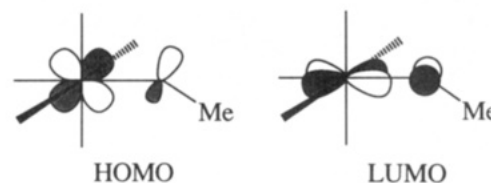


Figure 2. Frontier orbitals for 10. Coefficients are from the extended Hückel calculations described in the text. (Orbitals of ancillary carbonyl ligands are omitted for clarity.)

methanol is observed in the system,¹⁸ and decomposition of zwitterion 3 in the presence of methanol fails to increase the amount of 9.

The inorganic product of the decomposition of 3 is the low-valent nitrene complex (CO)₅W=NPh (5). While 5 has not been isolated or detected spectroscopically, the formation of phosphine ylide 6 upon generation of 5 in the presence of PPh₃ is evidence for its transient existence.²

Electronic Structure of 5. The scarcity of characterized low-valent nitrene complexes may be due to reduced metal-nitrene ligand bonding, as compared to their high-valent counterparts. In high-valent imido complexes, donation of the nitrogen lone pair to the electron-deficient metal center forms a formal metal-nitrogen triple bond, as evidenced by the linear imido ligand.¹⁹ In contrast, application of the EAN rule to 5 indicates that in order to avoid exceeding 18 electrons on the metal, the nitrene ligand must be doubly bonded to the metal. Therefore, 5 is predicted to possess a bent nitrene ligand.³

In order to further understand the bonding and electronic structure of complexes such as (CO)₅W=NPh (5), extended Hückel molecular orbital calculations²⁰ were carried out on the model compound, (CO)₅W=NMe (10), and on its constituent

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(10) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190-8192.

(11) (a) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263-1267. (b) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194-9198. (c) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665-3668. (d) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83-101.

(12) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* **1991**, *10*, 541-543.

(13) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411-432. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587-608. (c) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137-144. (d) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433-445.

(14) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282-7292.

(15) Subsequent to the report of zwitterion 3, there have been two other reports of similar species. Brookhart and Templeton have reported the reaction of (η⁵-C₅H₅)(CO)₂Fe=CH(p-C₆H₄OMe)⁺ with azobenzene to produce the intermediate (η⁵-C₅H₅)(CO)₂FeNPhNPhCH(p-C₆H₄OMe)⁺.¹⁶ Likewise, Hegedus has reexamined the previously reported^{11a} reaction of (CO)₅Cr=C(OCH₃)CH₃ with azobenzene and has detected the chromium congener of zwitterion 3 by ¹H NMR.^{11b}

(16) Peng, W.-J.; Gamble, A. S.; Templeton, J. L.; Brookhart, M. *Inorg. Chem.* **1990**, *29*, 463-467.

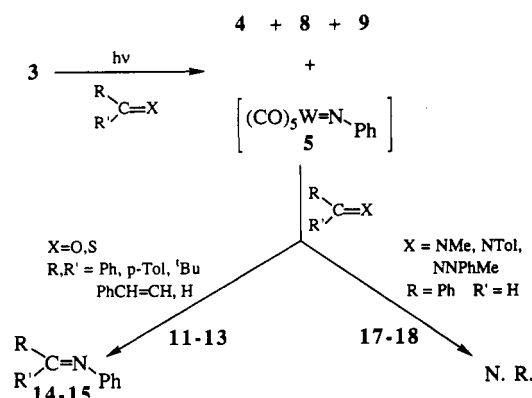
(17) An authentic sample was prepared through the reaction of phenyl isocyanate with methanol.

(18) Isocyanates cannot be observed by NMR or IR in the reaction mixtures. Traces of free isocyanate can be detected by GC/MS but may be produced by pyrolysis in the injection port.

(19) There is at least one exception in which the extra pair of electrons from a linear imido ligand resides in a nonbonding nitrogen-centered MO. Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642-1643.

(20) Extended Hückel calculations were carried out by using the program FORTICON8, obtained from QCPE as program QCMP011. Weighted H_{ij}'s were used, and the parameters for W were taken from ref 21.

Scheme II



fragments $\text{W}(\text{CO})_5$ and NMe. The geometry of the $\text{W}(\text{CO})_5$ fragment was taken from the X-ray structure of $(\text{CO})_5\text{W}=\text{CPh}(\text{OMe})$.²² The $\text{W}=\text{N}$ bond length (1.79 Å) and $\text{W}-\text{N}-\text{R}$ bond angle (139°) used were those found in the only structurally characterized complex with a strongly bent imido ligand, $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$.²³ Figure 1 shows the resulting partial molecular orbital diagram.

Overlap of the metal d_{xz} and d_{yz} orbitals with p_x and p_y on nitrogen forms the π -system of the $\text{W}-\text{N}$ bond. The occupied d_{xz} orbital on the metal donates electron density into the empty p_x orbital on nitrogen. In addition, interaction of the doubly occupied d_{yz} orbital on $\text{W}(\text{CO})_5$ and p_y orbital on NMe generates filled " π " and " π^* " orbitals. Although the nodal patterns of these orbitals are similar to those of π bonds, they are not rigorously of π symmetry, as the bending of the nitrene ligand gives these orbitals a σ component.

The highest occupied molecular orbital (HOMO) of the complex is the " π^* " orbital lying in the yz plane, while the π^* orbital in the xz plane is the lowest unoccupied molecular orbital (LUMO) (Figure 2). These two orbitals are similar in energy, their degeneracy being broken by the bending of the NMe ligand.

The HOMO and LUMO of $(\text{CO})_5\text{W}=\text{NMe}$ lie close in energy and are also well-separated from other orbitals. The availability of the frontier orbitals suggests that this low-valent nitrene complex, and therefore the similar complex $(\text{CO})_5\text{W}=\text{NPh}$ (5), should be extremely reactive. In addition, the orbital picture resulting from these extended Hückel calculations implies that complexes of the type $(\text{CO})_5\text{W}=\text{NR}$ could react with both electrophiles and nucleophiles. Such ambiphilic behavior has previously been reported for some metal carbenes,²⁴ but to our knowledge ambiphilic reactivity at nitrogen is unprecedented for transition-metal nitrene, or imido, complexes.²⁵ This picture of 5 as ambiphilic is supported by its reactivity with nucleophilic PPh_3 and electrophilic species such as aldehydes, ketones, and thioketones (vide infra).

Reaction of 5 with Carbonyl Compounds. To probe the nucleophilicity of the low-valent nitrene complex 5, the photochemical decomposition of 3 was performed in the presence of aldehydes, ketones, and thioketones 11–13. Under these conditions, the previously observed products of zwitterion 3 decomposition, 4, 8, and 9, were again present in similar yields as well as the *N*-phenyl imines (14 and 15) of the carbonyl compounds (Scheme II and Table I).

The kinetics of decomposition of 3 in the presence of benzaldehyde were monitored under the photochemical reaction conditions. ^1H NMR monitoring showed the disappearance of

Table I

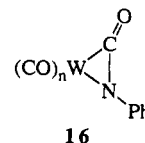
Substrate	Equiv. ^a	Product	Yield (%) ^b
11a $\begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{H} \end{array}$	1.3 1.3	14a $\begin{array}{c} \text{NPh} \\ \parallel \\ \text{Ph}-\text{C}-\text{H} \end{array}$	84 81 ^c
11b $\begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{CH}=\text{C}-\text{H} \end{array}$	1.0	14b $\begin{array}{c} \text{NPh} \\ \parallel \\ \text{Ph}-\text{CH}=\text{C}-\text{H} \end{array}$	77 ^d
11c $\begin{array}{c} \text{O} \\ \parallel \\ t\text{Bu}-\text{C}-\text{H} \end{array}$	1.5	14c $\begin{array}{c} \text{NPh} \\ \parallel \\ t\text{Bu}-\text{C}-\text{H} \end{array}$	65
12a $\begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-p\text{-Tol} \end{array}$	1.7 6.3	15a $\begin{array}{c} \text{NPh} \\ \parallel \\ \text{Ph}-\text{C}-p\text{-Tol} \end{array}$	3 13
12b $\begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{CH}=\text{C}-\text{Ph} \end{array}$	4.4	15b $\begin{array}{c} \text{NPh} \\ \parallel \\ \text{Ph}-\text{CH}=\text{C}-\text{Ph} \end{array}$	6 ^d
13 $\begin{array}{c} \text{S} \\ \parallel \\ \text{Ph}-\text{C}-p\text{-Tol} \end{array}$	5.5 3.0	15a $\begin{array}{c} \text{NPh} \\ \parallel \\ \text{Ph}-\text{C}-p\text{-Tol} \end{array}$	48 ^c 27 ^c

^a Ratio of substrate to zwitterion 3 in solution. ^b NMR yield, unless otherwise indicated, of imine with respect to 3. ^c Isolated yield. ^d Includes both free imine and its $(\text{CO})_5\text{W}$ coordinated adduct.

zwitterion 3 to be first order in the concentration of 3 and independent of benzaldehyde concentration. This supports the initial unimolecular decomposition of 3 to produce imidate 4 and $(\text{CO})_5\text{W}=\text{NPh}$ (5), followed by a reaction of 5 with 11–13 to produce imines 14 and 15.

Control experiments have demonstrated that imines 14 and 15 produced in this reaction are not the result of the transfer of NPh moieties from the organic metathesis products, imidate 4 and coordinated imidate 8. Additional control experiments ruled out aniline or azobenzene as a source of the NPh moiety in the product imines. Although previously generated low-valent nitrene complexes have been found to yield aniline and azobenzene in the final reaction mixtures,¹¹ these products were only detected in trace amounts (<2% by NMR) when 3 was allowed to decompose in the absence of trapping agents. While aniline does react with aldehydes and thioketones, it does not react with benzophenone (12a) or chalcone (12b) to produce imines under our reaction conditions. This result, coupled with the observed low yields of aniline and azobenzene in the decomposition of 3, eliminated the possibility of these compounds being the source of imine formation.

Additional control experiments addressed the question of isocyanate intermediates. The insertion of a carbonyl ligand into the metal–nitrogen bond of nitrene complex 5 would produce an isocyanate complex, 16. Though we have observed neither free nor complexed isocyanate in our system,¹⁸ isocyanate complexes have been reported as products of related reactions postulated to produce transient low-valent nitrene complexes.²⁶ In addition, metal carbonyls have been shown to catalyze the reaction of



isocyanates with aldehydes (but not ketones) to produce imines, presumably through the formation of intermediate isocyanate complexes.²⁷ Thus, phenyl isocyanate was photolyzed with the various carbonyl compounds in the presence of $\text{W}(\text{CO})_6$. Under these conditions, the aldehydes did react to produce imines, though

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 (22) Mills, O. S.; Redhouse, A. D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1082.

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(25) $(\text{Me}_3\text{SiO})_2\text{Cr}(\text{N}^t\text{Bu})_2$ reacts with both benzaldehyde⁵ and Ph_2Zn ,⁹ but the authors attribute the Ph_2Zn reaction to initial formation of a chromium aryl species followed by insertion.

(26) (a) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430–5437. (b) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8–11.

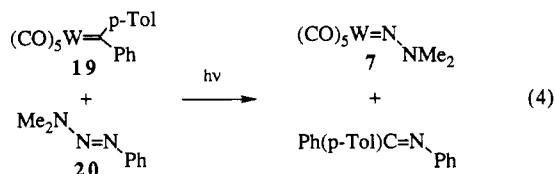
(27) Drapier, J.; Hoornaerts, M. T.; Hubert, A. J.; Teyssie, P. J. *Mol. Catal.* **1981**, *11*, 53–68.

at a much slower rate than observed in the reaction of **5**. In contrast, benzophenone exhibited no $W(CO)_6$ -catalyzed reaction with the isocyanate. This provides strong evidence against the intermediacy of isocyanates in the formation of imines **14** and **15**.

These data are consistent with production of imines **14** and **15** through the reaction of carbonyl compounds **11–13** with the low-valent nitrene complex **5** (eq 2). This reaction is similar to those previously observed in high-valent imido complexes.^{3c,4}

Table I shows that aldehydes **11a–c** produce a noticeably greater amount of imine than ketones **12a,b** or thioketone **13**. Competition between decomposition of **5** and its reaction with **11–13** is believed to be the reason for the difference in yields. The trend of imine yields in Table I is consistent with the relative susceptibility of the carbonyl compounds to attack by nitrogen nucleophiles, as illustrated by the faster reaction of aniline with aldehydes than with ketones.²⁸ Thus, the formation of imine is faster than decomposition of **5** in the reaction with aldehydes (**11**), while the less reactive ketones (**12**) and thioketones (**13**) give much lower yields of imine. Similarly, increasing the concentration of ketone **12a** or thioketone **13** results in a proportional increase in observed imine (Table I). Nitrene complex **5** was found not to react with $MeN=CHPh$ (**17a**), $p-TolN=CHPh$ (**17b**), or $Ph(Me)NN=CHPh$ (**18**) (Scheme II), presumably due to the reduced electrophilicity of these substrates as compared to **11–13**.

Comparison of the Reactivity of 5 and $(CO)_5W=NNMe_2$ (7). Metathesis between $(CO)_5W=C(p-Tol)Ph$ (**19**) and the triazene $PhN=NNMe_2$ (**20**) yields the dimethylamino-substituted nitrene complex $(CO)_5W=NNMe_2$ (**7**) (eq 4).¹² In contrast to the



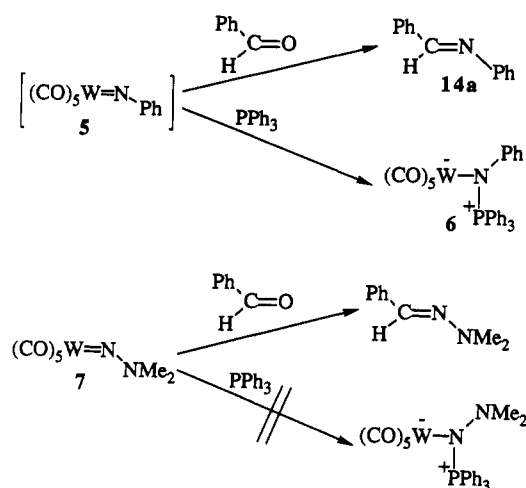
unstable phenyl substituted nitrene **5**, which has thus far avoided detection, **7** has been observed and characterized spectroscopically. Preliminary studies have indicated that the donor substituent on the nitrene nitrogen of **7** not only affects this compound's stability, but its reactivity as well. As opposed to nitrene complex **5**, **7** was found not to add PPh_3 at the nitrene nitrogen at room temperature. However, **7** does react with the electrophile benzaldehyde to produce the hydrazone $Me_2NN=CHPh$ in 85% yield (Scheme III).

The failure of **7** to form a phosphine ylide analogous to **6** implies reduced electrophilicity of the donor-substituted nitrene nitrogen as compared to that in **5**. This situation is parallel to that observed with Fischer carbenes: while PPh_3 reacts readily ($-78^\circ C$) with the highly electrophilic non-heteroatom-substituted carbene $(CO)_5W=CHPh$ to give a phosphine ylide,¹⁴ heteroatom-stabilized Fischer carbenes such as $(CO)_5W=C(OMe)Me$ do not add PPh_3 at the carbene carbon, even at room temperature.²⁹ This can be attributed to donation of π -electron density from the heteroatom onto the carbene carbon. Likewise, it appears donation from the dimethylamino substituent onto the nitrene nitrogen of **7**, as evidenced by restricted rotation about the N–N bond,¹² effectively decreases the electrophilicity of this complex. The reaction of **7** with benzaldehyde confirms this compound can react as a nucleophile similar to **5**. However, the ambiphilic behavior observed in **5** does not have an exact parallel in **7**. These results are summarized in Scheme III.

Inorganic Product of Reaction of 5 with Carbonyl Compounds.

While the organic products of the reaction of nitrene complexes **5** and **7** with organic carbonyl compounds, i.e., imines, have been well-characterized, the inorganic products of these transformations are as yet unknown. High-valent imido complexes have been shown to react with organic carbonyl compounds to produce imines and high-valent oxo complexes (eq 3). The corresponding low-valent oxo complex, $(CO)_5W=O$ (**21**), has not been detected in

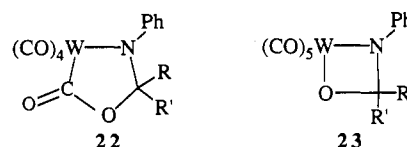
Scheme III



our system. Rather, the decomposition of **3** in the presence of benzaldehyde results in the evolution of CO_2 , even at temperatures as low as $-78^\circ C$.

The formation of carbon dioxide is presumably the result of coupling of the benzaldehyde oxygen with a metal carbonyl ligand. Oxo complex **21** is a possible precursor to this coupling. In contrast to high-valent transition-metal oxo complexes, low-valent oxos such as **21** are predicted to be unstable, due to π -antibonding between filled metal d orbitals and oxygen lone pairs.³⁰ This instability could be alleviated by the insertion of a carbonyl ligand into the tungsten–oxo bond. The formation of CO_2 could then provide the thermodynamic driving force for the reaction of **5** with **11–13** as well.³¹

Alternatively, the high-energy low-valent oxo complex **21** could be avoided by the formation of a metallacyclic intermediate such as **22**. Such a species could arise from a number of pathways, including carbonyl insertion into **23**, the product of formal $[2 + 2]$ cycloaddition of **5** and the aldehyde or ketone. The fragmentation of **22** would also result in the formation of imine and CO_2 . Presently, we have no data to distinguish between these mechanisms.



Conclusion

The reaction of **5** and **7** with organic carbonyl compounds represents a new mode of reactivity for low-valent nitrene complexes. Although our data do not allow us to distinguish among the mechanistic possibilities for imine formation, the products observed in these reactions support the participation of complexes **5** and **7** as nucleophiles. The electronic structure of model compound **10**, as obtained from extended Hückel calculations, suggests that nitrene complexes of the type $(CO)_5M=NR$ should react as both nucleophiles and electrophiles. The reaction of **5** with carbonyl compounds, together with the previously reported reaction of **5** with PPh_3 ,² confirm the ambiphilic nature of $(CO)_5W=NPh$. Such ambiphilic behavior is to our knowledge unprecedented for transition-metal nitrene and imido complexes, which typically exhibit either electrophilic or nucleophilic behavior.³²

The transfer of the NPh moiety to aldehydes, ketones, and thioketones demonstrates that low-valent nitrene complexes can

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be used to incorporate nitrene ligands into organic species. Unfortunately, the decomposition of complex **5** appears to be a very favorable process and has thus far stymied the generalization of this reaction, as shown by the low yields of imines with ketones, and no reaction of **5** with imines **17** and hydrazone **18**. Similarly, the photolysis of **3** in the presence of various olefins has only yielded nitrene decomposition products.³³ The synthesis of a more stable and isolable low-valent nitrene complex may significantly slow the decomposition pathway and allow for the reaction of these complexes with other substrates.

Experimental Section

General Methods. Standard inert atmosphere techniques were used in all of these experiments. Diethyl ether and toluene were distilled from sodium/benzophenone. Hexane, petroleum ether, *n*-pentane, chloroform, and methylene chloride were distilled from CaH_2 . All NMR solvents were degassed by 3 freeze-pump-thaw cycles. Benzene- d_6 and toluene- d_8 were vacuum transferred from sodium/benzophenone. CDCl_3 and CD_2Cl_2 were stored over 3 Å molecular sieves. All other reagents were purchased in reagent grade and used with no further purification.

^1H and ^{13}C spectra were recorded on a Varian XL-400 NMR spectrometer. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. Analytical gas chromatography (GC) was performed on an HP5890A chromatograph containing a 5 m $\times$ 0.25 mm column of SE-54 on fused silica. Gas chromatography/mass spectrometry (GC/MS) was performed on a Hewlett-Packard 5890 or 5970 gas chromatograph/mass spectrometer containing a 25 m $\times$ 0.20 mm column of SE-30 on fused silica, 100% cross-linked methyl.

Unless otherwise stated, all photolyses were performed in 5-mm NMR tubes by irradiation with a Hanovia medium-pressure mercury vapor lamp in a Pyrex immersion well.

Pentacarbonyl[(methoxy)(methyl)carbene]tungsten (**1**),³⁴ *cis*-azobenzene (**2-C**),³⁵ methyl *N*-phenylacetimidate (**4**),³⁶ *p*-tolyl phenyl thioketone (**13**),³⁷ *N*-benzylidene methyl amine (**17a**),³⁸ and pentacarbonyl[(*p*-tolyl)(phenyl)carbene]tungsten (**19**)³⁹ were prepared by literature methods. Benzaldehyde methylphenylhydrazone (**18**) and benzaldehyde dimethylhydrazone were prepared by standard methods from benzaldehyde and the appropriate hydrazine. Methyl *N*-phenylcarbamate (**9**) was prepared from phenyl isocyanate and methanol. Authentic samples of imines (**14** and **15**) were prepared via the condensation of the appropriate carbonyl compound with freshly distilled aniline in a toluene solution containing 3 Å molecular sieves.

Synthesis of $(\text{CO})_5\text{WNPhNPhC(OMe)Me}$ (3**).** Tungsten carbene **1** (130 mg, 0.38 mmol) was added to *cis*-azobenzene (**2-C**) (68 mg, 0.38 mmol) in 2 mL of CH_2Cl_2 or C_6H_6 . The solution turned dark red immediately. After 2–3 min in the dark, solvent was removed in vacuo. The resulting dark red residue was purified by washing with pentane until the decanted pentane solutions were clear. The residue was dried in vacuo (2–3 minutes) to yield **3** (161 mg, 0.29 mmol, 75% yield). Solutions of **3** were completely decomposed after standing for 24 h, in the dark at room temperature: ^1H NMR (C_6D_6) δ 1.64 (s, 3 H), 2.45 (s, 3 H), 6.68 (t, 1 H), 6.82 (d, 2 H), 6.93 (m, 3 H), 7.20 (t, 2 H), 7.27 (d, 2 H); IR (KBr) ν_{WCO} 2061 (m), 1913 (vs), 1860 (s) $\nu_{\text{C=N}}$ 1590 cm^{-1} . Additional spectral data for **3** can be found in ref 1.

Photochemical Decomposition of **3.** Zwitterion **3** (85 mg, 0.15 mmol) was dissolved in toluene- d_8 (0.5 mL) with TMS as reference. The solution was placed in an NMR tube and photolyzed at room temperature for a period of 3 h. ^1H NMR of this solution showed the complete disappearance of **3** and the formation of the following products. Imidate $\text{PhN}=\text{C}(\text{OCH}_3)\text{CH}_3$ (**4**): ^1H NMR (C_6D_6) δ 1.58 (s, 3 H, CH_3), 3.63 (s, 3 H, OCH_3); NMR yield 70%. Imidate complex $(\text{CO})_5\text{W}[\text{PhN}=\text{C}(\text{OCH}_3)\text{CH}_3]$ (**8**): ^1H NMR (C_6D_6) δ 0.84 (s, 3 H, CH_3), 2.90 (s, 3 H, OCH_3); NMR yield 14%. Carbamate $\text{PhNH}(\text{CO})\text{OCH}_3$ (**9**): ^1H NMR (C_6D_6) δ 3.41 (s, 3 H, OCH_3); NMR yield 10%. Assignments were made upon comparison with authentic samples.

The phenyl region is complex, with a broad peak underneath the multiplets corresponding to the imidates and carbamate (δ 6.5–7.6). This broad peak appears in all ^1H NMR spectra of mixtures that generate **5** without trapping reagents present. GC/MS of the reaction mixture showed a trace of phenyl isocyanate [M^+ , (100%), 119], aniline [M^+ ,

(100%), 93], imidate **4** [M^+ , (65%), 149], and azobenzene **2** [$(\text{M} - 105)^+$, (100%), 77].

Thermal Decomposition of **3.** Zwitterion **3** (60 mg, 0.11 mmol) was dissolved in 0.5 mL of benzene- d_6 , and the ^1H NMR spectra were recorded. The solution was allowed to sit for 19 h at room temperature in the dark. ^1H NMR spectra showed complete disappearance of **3** and the formation of a complex mixture, including imidate **4** (12%), imidate complex **8** (<1%), carbamate **9** (17%), and azobenzene (16%) as well as other unidentified material.

Photolysis of **3 in the Presence of **11–13**, **17**, and **18**.** A typical procedure follows: Zwitterion **3** (126 mg, 0.22 mmol) was dissolved in benzene- d_6 (2 mL), and benzaldehyde (33 mg, 0.31 mmol) added. The solution was transferred to an NMR tube, and the ^1H NMR spectra were recorded. The solution was then photolyzed for 3 h. ^1H NMR spectra of this solution showed the complete disappearance of **3**, and the formation of a new product at δ 8.13 (s, 1 H), δ 7.82 (d, 2 H). Comparison with an authentic sample showed this product to be benzaldehyde anil **14a**. The NMR yield of **14a** was calculated to be 84% based on initial **3**.

Evaporation of solvent left a brown oil, which was dissolved in diethyl ether (4 mL) and filtered through neutral alumina to remove tungsten material. Diethyl ether was removed in vacuo, and the orange oil was evacuated down to 50 μm to remove all volatile compounds (e.g., imidate **4**). ^1H NMR and GC showed the oil to be 95+% pure imine (33 mg, 81% isolated yield).

Reaction of Aniline with **11b, **12a**, and **13**.** A typical procedure follows: Aniline (7.1 mg, 0.076 mmol) was dissolved in 0.5 mL of benzene- d_6 and added to cinnamaldehyde (**11b**) (8 mg, 0.06 mmol) and $\text{W}(\text{CO})_6$ (5 mg, 0.014 mmol). The solution was transferred to an NMR tube, and the ^1H NMR spectra were recorded. The NMR tube was photolyzed for 2.5 h, followed by another ^1H NMR.

Cinnamaldehyde (**11b**) and thioketone **13** produced imines **14b** (65% yield, ^1H NMR) and **15a** (<5% yield, ^1H NMR) respectively, while ketone **12a** produced no imine **15a**.

Reaction of Azobenzene with **11b and **13**.** A typical procedure follows: Thioketone **13** (15 mg, 0.071 mmol) was added to azobenzene (6.5 mg, 0.035 mmol) and $\text{W}(\text{CO})_6$ (5 mg, 0.014 mmol) in 0.5 mL of benzene- d_6 . The solution was placed in an NMR tube, and the ^1H NMR spectra were recorded. The solution was photolyzed for 2 h, followed by another ^1H NMR.

No imine was produced for either **11b** or **13** in this reaction.

Reaction of Phenyl Isocyanate with **11b and **12a**.** A typical procedure follows: Cinnamaldehyde (**11b**) (20 mg, 0.15 mmol) was dissolved in 0.5 mL of benzene- d_6 and added to phenyl isocyanate (12 mg, 0.11 mmol) and $\text{W}(\text{CO})_6$ (10 mg, 0.028 mmol). The solution was transferred to an NMR tube, and the ^1H NMR spectra were recorded. The solution was photolyzed for 2 h, followed by the recording of another ^1H NMR.

Cinnamaldehyde (**11b**) was found to produce traces of imine **14b** (3% by ^1H NMR), while 4-methylbenzophenone (**12a**) yielded no imine **15a**.

Reaction of Imidate **4 with **11b** and **13**.** A typical procedure follows: Thioketone **13** (15 mg, 0.071 mmol) was added to imidate **4** (15.5 mg, 0.10 mmol) and $\text{W}(\text{CO})_6$ (5 mg, 0.014 mmol) in 0.5 mL of benzene- d_6 . The solution was placed in an NMR tube, and the ^1H NMR spectra were recorded. The solution was photolyzed for 2 h, followed by another ^1H NMR.

Neither **11b** nor **13** was observed to produce any imine by ^1H NMR.

Evolution of CO_2 . Zwitterion **3** (200 mg, 0.44 mmol) was dissolved in 8 mL of toluene, and the solution was divided equally into two 25-mL round-bottomed flasks, equipped with stir bars and septa. To one flask was added benzaldehyde (53 mg, 0.50 mmol). Each flask was then equipped with a nitrogen purge line and a cannula connecting the flasks to two separate 10-mL solutions of concentrated $\text{Ba}(\text{OH})_2$. The nitrogen purge lines were turned on, and the head gases of the reaction flasks were bubbled through the $\text{Ba}(\text{OH})_2$ solutions. Both reaction flasks were photolyzed at room temperature for 3 h. After photolysis, the $\text{Ba}(\text{OH})_2$ solution connected to the solution containing **3** and benzaldehyde contained a white precipitate, BaCO_3 , which evolved a gas (CO_2) upon addition of concentrated HCl. The $\text{Ba}(\text{OH})_2$ solution connected to the solution of **3** was clear.

Kinetics of Photochemical Decomposition of **3.** A 3-mL toluene- d_8 solution of **3** (100 mg, 0.18 mmol) was prepared and divided evenly into three NMR tubes. To one tube was added 1.7 equiv of benzaldehyde (11 mg, 0.10 mmol) and to another 6.6 equiv of benzaldehyde (43 mg, 0.40 mmol). These three solutions were photolyzed for periods of 10 min totaling 0.5 h, and the decomposition of **3** was monitored by ^1H NMR. The rate of disappearance of **3** was the same in the absence of benzaldehyde as in its presence at either concentration.

Generation of $(\text{CO})_5\text{W}=\text{NNMe}_2$ (7**).** Triazene **20** (15 mg, 0.10 mmol) was dissolved in 0.5 mL of CDCl_3 and added to tungsten carbene **19** (32 mg, 0.066 mmol). The solution was placed in an NMR tube,

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cooled to $-40\text{ }^{\circ}\text{C}$, and photolyzed with Pyrex-filtered light at $-40\text{ }^{\circ}\text{C}$ for 40 min. The ^1H NMR of the resulting mixture (CDCl_3) showed the formation of $\text{Ph}(p\text{-Tol})\text{C}\equiv\text{NPh}$ in 94% yield as well as nitrene complex **7** (δ 3.83, s, 6 H) in 66% yield. Complex **7** was found to persist for several hours in solution. Additional spectroscopic data for **7** (variable-temperature ^1H NMR, ^{13}C NMR, ^{15}N NMR, and IR) are reported and discussed in detail in ref 12. The original spectra for **7** are also available in the supplementary material of ref 12.

Reaction of 7 with Benzaldehyde. Carbene **19** (16 mg, 0.033 mmol) in 0.5 mL of toluene- d_6 was added to triazene **20** (25 mg, 0.17 mmol). The solution was transferred to an NMR tube and photolyzed at $-40\text{ }^{\circ}\text{C}$ with Pyrex-filtered light for 40 min. ^1H NMR of the resulting mixture showed the appearance of **7** (δ 2.77, s, 6 H). An excess of benzaldehyde

(50 mg, 0.47 mmol) was added to this solution, and the mixture was allowed to stand in the dark at room temperature for 13 h. ^1H NMR spectra of the resulting solution showed the disappearance of **7**, and the formation of $\text{PhHC}\equiv\text{NNMe}_2$ (δ 2.65, s, 6 H) in 85% yield.

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Preparation and Spectroscopic Properties of the η^2 -Dihydrogen Complexes $[\text{MH}(\eta^2\text{-H}_2)(\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2]^+$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{R} = \text{Ph}, \text{Et}$) and Trends in Properties down the Iron Group Triad

Maria T. Bautista, E. Paul Cappellani, Samantha D. Drouin, Robert H. Morris,*
Caroline T. Schweitzer, Andrea Sella, and Jeffery Zubkowski

Contribution from the Department of Chemistry and the Scarborough Campus, University of Toronto, Toronto, Ontario M5S 1A1, Canada. Received October 19, 1990

Abstract: Complexes $\text{trans-}[\text{M}(\text{H})(\eta^2\text{-H}_2)\text{L}_2]\text{BF}_4$ ($\text{L} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2 = \text{dppe}$ (**1Fe**, **1Ru**), $\text{PEt}_2\text{CH}_2\text{CH}_2\text{PEt}_2 = \text{depe}$ (**2Ru**)) are prepared by reaction of $\text{cis-M}(\text{H})_2\text{L}_2$ with 1 equiv of $\text{HBF}_4\cdot\text{Et}_2\text{O}$. Deprotonation of **1Ru** by BuLi at 200 K, gives thermally unstable $\text{trans-Ru}(\text{H})_2(\text{dppe})_2$, which isomerizes to $\text{cis-Ru}(\text{H})_2(\text{dppe})_2$. Tetraphenylborate salts of the complexes **1Fe**, **2Fe**, and **2Ru** are prepared by reaction of $\text{trans-M}(\text{Cl})(\text{H})\text{L}_2$ with NaBPh_4 under 1 atm of H_2 . **2Fe**, **1Ru**, and **2Ru** can also be made directly from the complexes $\text{cis-MCl}_2\text{L}_2$ by reaction with 1 atm of H_2 , excess NaBPh_4 , and 1 equiv of NaOEt (or NaOtBu) in THF. Some properties of the complexes $[\text{Os}(\text{H})(\text{H}_2)(\text{L})_2]^+$ ($\text{L} = \text{dppe}$ (**1Os**), depe (**2Os**)) are included to reveal trends down the triad of metals; $\text{ReH}_3(\text{dppe})_2$ also provides useful comparisons. The terminal hydride stretching mode, $\nu(\text{M-H})$, increases in frequency as $\text{Fe} < \text{Ru} < \text{Os}$, and the ^{31}P chemical shifts increase in the order $\text{Fe} < \text{Ru} < \text{Os}$ as expected for isostructural complexes. However, indicators of dihydrogen vs dihydride character show that Ru is out of place in the periodic order. ^1H NMR spectra of isotopomers $\text{trans-}[\text{M}(\text{H})(\eta^2\text{-HD})\text{L}_2]^+$ and $\text{trans-}[\text{M}(\text{D})(\eta^2\text{-HD})\text{L}_2]^+$ give couplings $^1J(\text{H,D})$ that decrease as $\text{Ru} > \text{Fe} > \text{Os}$. The chemical shifts of the HD for these two isotopomers are quite different because of the higher trans influence of D than H. The chemical shift difference, $\delta(\text{dihydrogen}) - \delta(\text{terminal hydride})$, for complexes **1** and **2** also decreases as $\text{Ru} > \text{Fe} > \text{Os}$. The T_1 values of the dihydrogen nuclei, $T_1(\text{H}_2)$, and the hydride ligand, $T_1(\text{H})$, were determined over the temperature range of 190–300 K for the complexes **2Fe** and **2Ru** in acetone- d_6 . Analysis of these and other data suggests H–H distances for the rapidly spinning H_2 ligand of the Fe and Ru complexes are comparable at $0.87 \pm 0.02\text{ \AA}$. An overall ordering of increasing distances is $\text{Ru} \approx \text{Fe} < \text{Os}$. The lability of dihydrogen as judged by the qualitative H_2/D_2 rates of exchange increases as $\text{Os} < \text{Fe} < \text{Ru}$. The equilibrium constant for H_2 binding and hence the strength of the H_2 –metal bond likely increases as $\text{Ru} < \text{Fe} < \text{Os}$. Thus, the Ru complexes have the strongest H–H interaction and weakest metal–dihydrogen interaction. The $[\text{RuHL}_2]^+$ unit is a poorer π -back-bonder than the corresponding complexes of either Fe or Os and forms weaker σ -bonds than Os. Electrochemical and infrared data both indicate that the ease of oxidation of the binding sites for N_2 and Cl^- decreases as $\text{ReH}(\text{dppe})_2 \gg [\text{FeH}(\text{depe})_2]^+ > [\text{FeH}(\text{dppe})_2]^+ > [\text{MH}(\text{depe})_2]^+ > [\text{MH}(\text{dppe})_2]^+$ ($\text{M} = \text{Ru}, \text{Os}$). H atom exchange between H_2 and hydride ligands is monitored by variable-temperature ^1H NMR, and spectra are simulated to give $\Delta G^\ddagger$ values that decrease as $\text{Ru} > \text{Fe} > \text{Os}$ and $\text{dppe} > \text{depe}$. This exchange likely proceeds via the homolytic cleavage of the H–H bond.

Introduction

Since the report of the first η^2 -dihydrogen complexes,^{1,2} many transition-metal complexes, both stable^{3–21} and unstable^{18,22,23} at

room temperature, have been identified as containing hydrogen ligands with H–H bonding interactions. This is a study of how

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