

$w = 1/\sigma^2(F_o)$ . A difference Fourier map calculated in the final stages of refinement revealed the positions of all hydrogen atoms in the structure. These were included in the final cycles of refinement with isotropic temperature factors set at  $H_{iso} = [1.5 + C_{iso} - H]$ . Neutral atomic scattering factors and anomalous dispersion corrections for Ru and Mo atoms used were those tabulated in ref 11. The  $R$  indices and refinement parameters are given in Table III. The final positional and thermal parameters of VII are listed in Table V, and selected interatomic distances and angles are given in Table IV. A complete listing of the observed and calculated structure factor amplitudes, anisotropic

thermal parameters, and bond distances and angles are available as supplementary material.

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**Registry No.** I, 84802-27-7; II, 84802-26-6; III, 12194-13-7; IV, 112840-69-4; V, 112840-70-7; VI, 112840-72-9; VII, 112840-71-8; [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub>, 12091-64-4; [Ru<sub>3</sub>( $\mu_3$ - $\eta^2$ -C<sub>2</sub>-*t*-Bu)(CO)<sub>9</sub>]( $\mu$ -HgI), 74870-35-2; HRu<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>9</sub>, 72942-48-4; HRu<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)(CO)<sub>9</sub>, 57673-31-1; Ru<sub>3</sub>(CO)<sub>12</sub>, 15243-33-1.

**Supplementary Material Available:** Anisotropic thermal parameters (Table VI) and bond distances and angles (Table VII) (4 pages); a complete listing of the observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

(10) CRYGLS, local crystallographic least-squares program. All computational work was performed on the CDC-Cyber 170/760 at the State University Data Center, Los Angeles, CA, and CSULA.

(11) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A. Cromer, D. T. *Ibid.* Table 2.3.1.

## Metal to Ligand Charge-Transfer Photochemistry of Metal-Metal Bonded Complexes. 5.<sup>†</sup> ESR Spectra of Stable Rhenium- $\alpha$ -Diimine and Spin-Trapped Manganese- $\alpha$ -Diimine Radicals

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Irradiation ( $\lambda \geq 320$  nm) of (CO)<sub>5</sub>MM'(CO)<sub>3</sub>L and Ph<sub>3</sub>SnM'(CO)<sub>3</sub>L (M, M' = Mn, Re; L =  $\alpha$ -diimine = 2,2'-bipyridine, 1,10-phenanthroline, pyridine-2-carbaldehyde imine, and 1,4-diaza-1,3-butadiene) leads to homolysis of the metal-metal bond yielding fairly stable solvated radicals SM'(CO)<sub>3</sub>L\*. These paramagnetic species have been studied by ESR spectroscopy in solution directly or by using nitroso-2,2-dimethylpropane as a spin-trapping reagent. The ESR spectra show extensive hyperfine splittings of the unpaired electron with the nuclei <sup>14</sup>N, <sup>1</sup>H, and <sup>55</sup>Mn or <sup>185,187</sup>Re. From the observed and computer-simulated coupling constants important information could be derived about the electronic structure of the singly occupied molecular orbital (SOMO). After in situ addition of P(OPh)<sub>3</sub>, P(OMe)<sub>3</sub>, or pyridine (= L') to Re(CO)<sub>3</sub>(*t*-Bu-DAB)\*, the new paramagnetic adducts axial-(L')Re(CO)<sub>3</sub>(*t*-Bu-DAB)\* could be identified.

### Introduction

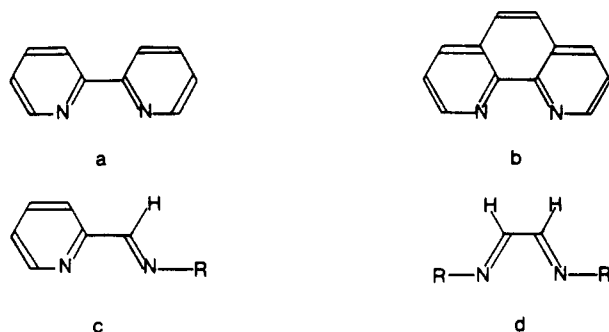
For many years organometallic reactions have been assumed to proceed via intermediates with 16 or 18 valence electrons.<sup>1</sup> Recently, however, many reactions have been found in which 17- or 19-valence-electron complexes are involved as intermediates.<sup>2,3</sup>

Thus, several ligand substitution reactions have been found to proceed much more rapidly when a small (anodic or cathodic) current was passed through the solution.<sup>2</sup> Alternatively, 17-electron metal-centered radicals such as M(CO)<sub>5</sub>, M(CO)<sub>4</sub>L, M(CO)<sub>3</sub>L<sub>2</sub> (M = Mn, Re), CpM'(CO)<sub>3</sub> (M' = Mo, W), CpFe(CO)<sub>2</sub>, and Co(CO)<sub>4</sub> have been prepared photochemically, mainly from their metal-metal bonded dimers.<sup>3-7</sup> Several of these radicals have been identified as intermediates using transient spectroscopic techniques<sup>8</sup> or as persistent radicals in solutions or low-temperature matrices.<sup>9</sup> Substitution reactions of 17-electron species provided kinetic evidence for associatively activated pathways with formation of 19-electron species as intermediates.<sup>9,9a,10</sup> Further evidence for the formation

of these 19-electron intermediates was provided by the electron-transfer reactions of these radicals.<sup>3,5-7,11</sup> Espe-

- (1) Tolman, C. A. *Chem. Soc. Rev.* 1972, 1, 337.
- (2) Kochi, J. K. *J. Organomet. Chem.* 1986, 300, 139.
- (3) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* 1986, 5, 215.
- (4) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.
- (5) Meyer, Th. J.; Caspar, J. V. *Chem. Rev.* 1985, 85, 187.
- (6) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* 1985, 63, 217.
- (7) Stiegman, A. E.; Tyler, D. R. *Acc. Chem. Res.* 1984, 17, 61.
- (8) (a) Yesaka, H.; Kobayashi, T.; Yasafuku, K.; Nagakura, S. *J. Am. Chem. Soc.* 1983, 105, 6249. (b) Rothberg, L. J.; Cooper, N. J.; Peter, K. S.; Vaida, V. *J. Am. Chem. Soc.* 1982, 104, 3536. (c) Hughey, IV, C. J. L.; Anderson, C. P.; Meyer, Th. J. *J. Organomet. Chem.* 1977, 125, C49. (d) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* 1985, 4, 42. (e) Hanckel, J. M.; Lee, K.; Rushman, P.; Brown, T. L. *Inorg. Chem.* 1986, 25, 1852. (f) Freedman, A.; Bersohn, R. *J. Am. Chem. Soc.* 1978, 100, 4116. (g) Bray, R. G.; Seidler, P. F., Jr.; Gethner, J. S.; Woodin, R. L. *J. Am. Chem. Soc.* 1986, 108, 1312. (h) Seder, T. A.; Church, S. P.; Weitz, E. *J. Am. Chem. Soc.* 1986, 108, 7518. (i) Poliakov, M.; Weitz, E. *Adv. Organomet. Chem.* 1986, 25, 277. (j) Moore, B. D.; Simpson, M. B.; Poliakov, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* 1984, 785. (k) Moore, B. D.; Poliakov, M.; Turner, J. J. *J. Am. Chem. Soc.* 1986, 108, 1819. (l) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* 1978, 100, 7259. (m) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* 1982, 104, 1842. (n) Junk, G. A.; Svec, H. J. *J. Chem. Soc. A* 1970, 2102.

<sup>†</sup> For part 4, see: Andréa, R. R.; de Jager, H. E.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* 1986, 316, C24.



**Figure 1.** Structure of the four  $\alpha$ -diimine ligands used: 2,2'-bipyridine (a); 1,10-phenanthroline (b); pyridine-2-carbaldehyde imine (c); 1,4-diaza-1,3-butadiene (d).

cially the photochemical disproportionation reactions of the metal-metal bonded carbonyls  $Mn_2(CO)_{10}$ ,  $Cp_2Mo_2(CO)_6$ , and  $Cp_2Fe_2(CO)_4$  showed that these 19-electron complexes are discrete intermediates with sufficient lifetimes to undergo bimolecular reactions. Yet these lifetimes are rather short, either because the complexes are strong reducing agents or because of their ligand lability when the 19th electron occupies a M-L antibonding orbital. Because of this, only a few of such radicals in which the 19th electron occupies an energetically unfavorable metal-ligand antibonding orbital have been observed spectroscopically.<sup>12</sup>

A drastic increase of stability occurs when one of the ligands of the radical has an unoccupied orbital, lower in energy than the M-L antibonding orbital. The extra electron will then reside on that ligand, and the metal will be an 18-electron center bonded to a radical anion. Such complexes have been prepared by (photo)chemical reaction of a metal-metal bonded complex with ligands possessing a low-energy  $\pi^*$  orbital such as *o*-quinones,<sup>13</sup>  $\alpha$ -diimines,<sup>14</sup> substituted pyridines,<sup>15</sup> or 2,3-bis(diphenylphosphino)-

(9) (a) Church, S. P.; Poliakov, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515. (b) Sijmons, M. C. R.; Sweany, R. L. *Organometallics* **1982**, *1*, 834. (c) Huber, H.; Kundig, E. P.; Ozin, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 5585. (d) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103. (e) McCullen, S. B.; Walker, H. K.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (f) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. (g) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775. (h) Tyler, D. R.; Goldman, A. S. *J. Organomet. Chem.* **1986**, *311*, 349.

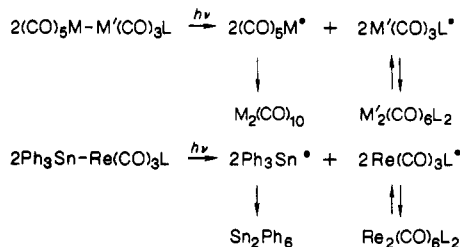
(10) (a) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (b) Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032. (c) Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (d) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700. (e) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (f) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (g) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1987**, *6*, 129. (h) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087.

(11) (a) Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434. (b) Stiegman, A. E.; Goldman, A. S.; Philbin, C. E.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2976.

(12) (a) Anderson, O. P.; Sijmons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1020. (b) Lionel, T.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *81*, 17. (c) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144.

(13) (a) Foster, T.; Chen, K. S.; Wan, J. K. S. *J. Organomet. Chem.* **1980**, *184*, 113. (b) Creber, K. A. M.; Ho, T.; Depew, M. C.; Weir, D.; Wan, J. K. S. *Can. J. Chem.*, **1982**, *60*, 1504. (c) Ho, T.; Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6524. (d) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101. (e) Creber, K. A. M.; Wan, J. K. S. *Chem. Phys. Lett.* **1981**, *81*, 453. (f) Creber, K. A. M.; Wan, J. K. S. *Can. J. Chem.* **1983**, *61*, 1017. (g) Chen, K. S.; Wan, J. K. S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 1726. (h) Creber, K. A. M.; Wan, J. K. S. *Transition Met. Chem. (Weinheim, Ger.)* **1983**, *8*, 253. (i) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1979**, *181*, 355.

(14) (a) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *241*, 313. (b) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *248*, 199.

Scheme I<sup>a</sup>

<sup>a</sup> M, M' = Mn, Re; L =  $\alpha$ -diimine.

maleic anhydride.<sup>16</sup> Alternatively, they have been prepared by (electro)chemical reduction of a complex already containing such a ligand with a low-energy  $\pi^*$  orbital.<sup>17</sup>

In the course of our study of the photochemistry of low-valence transition-metal complexes of the  $\alpha$ -diimine ligands 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), pyridine-2-carbaldehyde imine (R-PyCa,  $C_5H_4N-2-CH=NR$ ), and 1,4-diaza-1,3-butadiene (R-DAB,  $RN=CHCH=NR$ ) (Figure 1), reactions have been studied on a series of metal-metal bonded complexes.<sup>19</sup> The complexes  $(CO)_5MM'(CO)_3L$ ,  $(CO)_4CoM'(CO)_3L$ , and  $Ph_3SnRe(CO)_3L$  (M, M' = Mn, Re; L =  $\alpha$ -diimine) showed a homolytic splitting of the metal-metal bond upon irradiation into the low-energy metal to  $\alpha$ -diimine charge-transfer band. The  $M(CO)_5$ ,  $Co(CO)_4$ , and  $Ph_3Sn$  radicals thus formed react with each other to give the stable compounds  $Mn_2(CO)_{10}$ ,  $Co_2(CO)_8$ , and  $Sn_2Ph_6$ , respectively. Similarly, the  $M'(CO)_3L^*$  radicals form binuclear complexes  $M'_2(CO)_6L_2$  which are, however, partly split into their radical components. Only in the case of the  $Ph_3SnMn(CO)_3L$  complexes is homolysis of the metal-metal bond a minor reaction, the main reaction being the release of CO. The  $M'(CO)_3L^*$  radicals are in fact 16-electron species that easily form adducts with nucleophiles. Upon reaction of  $M'(CO)_3L^*$  with the basic phosphine  $P(n-Bu)_3$  the  $P(n-Bu)_3M'(CO)_3L^*$  adduct appears to be a very strong reductant.<sup>20</sup> It reduces the parent compound  $(CO)_5MnM'(CO)_3L$  to  $[Mn(CO)_5]^-$  and a new  $M'(CO)_3L^*$  radical, which starts a photocatalytic disproportionation reaction of the parent compound. This reaction is analogous to the photocatalytic disproportionation of  $Mn_2(CO)_{10}$  in pyridine.<sup>21</sup>

The ease of the formation of these  $M'(CO)_3L^*$  radicals for a variety of  $\alpha$ -diimine ligands and of their 18-electron adducts prompted us to study their electronic structures with ESR, in dependence of the metal,  $\alpha$ -diimine, and nucleophilic ligand used.

(15) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504.

(16) Fenske, D. *Chem. Ber.* **1979**, *112*, 363.

(17) (a) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187. (b) Franz, K. D.; tom Dieck, H.; Krynitz, U.; Renk, I. W. *J. Organomet. Chem.* **1974**, *64*, 361. (c) Franz, K. D.; tom Dieck, H.; Starzewski, K. A.; Hohmann, F. *Tetrahedron* **1975**, *31*, 1465.

(18) R-DAB stands for 1,4-disubstituted 1,4-diaza-1,3-butadiene  $RN=CH-CH=NR$ . Abbreviations used for R groups throughout the paper are as follows: *i*-Pr, isopropyl; *t*-Bu, *tert*-butyl; Me, methyl; Ph, phenyl; *p*-Tol, *p*-tolyl. For a complete review on the chemical properties of metal complexes containing a R-DAB ligand, see: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

(19) (a) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 2934. (b) Kokkes, M. W.; Snoeck, Th. L.; Stufkens, D. J.; Oskam, A.; Christophersen, M.; Stam, C. H. *J. Mol. Struct.* **1985**, *131*, 11. (c) Kokkes, M. W.; de Lange, W. G. J.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4411. (d) van Dyk, H. K.; Stufkens, D. J.; Oskam, A.; Rotteveel, M.; Heydenryk, D. *Organometallics* **1987**, *6*, 1665. (e) Andréa R. R.; de Lange, W. G. J.; Stufkens, D. J.; Oskam, A., submitted for publication.

(20) Kokkes, M. W.; de Lange, W. G. J.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1985**, *294*, 59.

(21) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527.

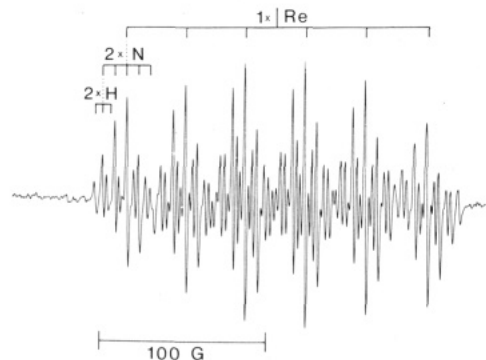


Figure 2. ESR spectrum of  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  (cyclohexane; 343 K).

### Results

Irradiation of  $(\text{CO})_5\text{MM}'(\text{CO})_3\text{L}$  ( $\text{M}, \text{M}' = \text{Mn}, \text{Re}$ ) or  $\text{Ph}_3\text{SnRe}(\text{CO})_3\text{L}$  in solution results in a homolytic splitting of the metal-metal bond and in the formation of radical species according to Scheme I.<sup>19</sup> Whereas  $\text{M}_2(\text{CO})_{10}$  and  $\text{Sn}_2\text{Ph}_6$  are stable compounds, not split into their radical components, the  $\text{M}'_2(\text{CO})_6\text{L}_2$  dimers may be partly split into  $\text{M}'(\text{CO})_3\text{L}^\bullet$  radicals, depending on the temperature and the stability of the dimer. Raising the temperature causes an increase in the radical concentration. The stability of the radicals with respect to the dimer strongly depends on the electronic and steric properties of L. Since the electron resides mainly in the lowest  $\pi^*$  level of L (vide infra), the energy of this orbital strongly influences the stability of the radical with respect to the dimer. The stability of the radical therefore increases in the order  $\text{bpy} < \text{R-PyCa} < \text{R-DAB}$ , which is the order of decreasing energy of the lowest  $\pi^*$  orbital of L.<sup>22</sup>

Finally, formation of the dimer is hampered by the presence of bulky substituents at the coordinating nitrogen atoms of L. This latter property has been used by Brown and co-workers to stabilize the  $^*\text{M}(\text{CO})_3(\text{PR}_3)_2$  ( $\text{M} = \text{Mn}, \text{Re}$ ) radicals.<sup>9d-e</sup> In view of these steric and electronic effects on the stability of the  $\text{M}'(\text{CO})_3\text{L}^\bullet$  radicals, we have concentrated our study on the  $\text{M}'(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  species, in which the R-DAB ligand possesses a bulky *t*-Bu group at each nitrogen atom. In the case of  $\text{M}' = \text{Mn}$  this complex appeared to be the only radical that could be studied with ESR without using a spin trap.

**ESR Spectra of the Radicals.** ESR spectra of the radicals have been obtained between 203 and 343 K, and they do not change character in this temperature region. Unfortunately, at still lower temperatures and from frozen solutions, no ESR signals could be obtained because of dimerization of the radicals.

The ESR spectrum of  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  in cyclohexane at 343 K, presented in Figure 2, shows extensive hyperfine splittings (hfs). The radical, which is stable for hours in the dark, exhibits six groups of multiplets arising from one  $^{185,187}\text{Re}$  nucleus ( $I = 5/2$ ), two equivalent  $^{14}\text{N}$  ( $I = 1$ ) nuclei, and two equivalent  $^1\text{H}$  ( $I = 1/2$ ) nuclei. Coupling constants due to  $^{185}\text{Re}$  and  $^{187}\text{Re}$  (37.5% and 62.5% natural abundance, respectively) cannot be distinguished from each other since their nuclear magnetic moments only differ by 1%. The computer-simulated coupling constants are collected in Table I.

The ESR spectrum of the corresponding  $\text{Mn}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  radical in toluene at 203 K is presented in Figure 3. All other  $\text{Mn}(\text{CO})_3\text{L}^\bullet$  ( $\text{L} = \text{bpy}, \text{phen}, \text{or } i\text{-Pr-PyCa}$ ) radicals were too unstable to be observed with ESR without using a spin-trapping reagent.

Table I. ESR Parameters<sup>a</sup> for  $\text{M}'(\text{CO})_3\text{L}^\bullet$  Radical Complexes

$\text{M}'$	$\alpha$ -diimine	solvent	$T, \text{K}$	$a_{\text{M}'}$	$a_{\text{N}}$	$a_{\text{H}}^b$	$g$
Re	<i>i</i> -Pr-DAB	cyclohexane	293	38.67	7.02	4.64 <sup>c</sup>	2.0051
		toluene	203	38.41	6.36	4.89	2.0059
	<i>t</i> -Bu-DAB	cyclohexane	343	35.55	7.34	5.03	2.0046
Re	<i>p</i> -tol-DAB	benzene	293	35.61	7.26	4.65	2.0036
		cyclohexane	343	36.60	5.30	4.08	2.0043
Re	<i>i</i> -Pr-PyCa	toluene	243	28.14	5.54 <sup>d</sup>	4.65 <sup>d</sup>	2.0051
Re	phen	toluene	203	20.88	3.60	2.99 <sup>e</sup>	2.0040
Mn	<i>t</i> -Bu-DAB	toluene	203	8.47	7.48	4.35	2.0043

<sup>a</sup> Coupling constants in gauss ( $\pm 0.05$ ). <sup>b</sup> Imine hydrogen. <sup>c</sup>  $a_{\text{H}}$  ( $\text{CH}_3\text{-CH-CH}_3$ ) = 1.63 G. <sup>d</sup> No inequivalence was observed between  $a_{\text{N}}/a_{\text{H}}$ (imine) and  $a_{\text{N}}/a_{\text{H}}$ (pyridine ring). <sup>e</sup>  $a_{\text{H}}$  of four ring protons.

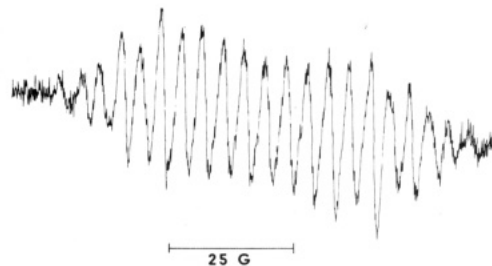


Figure 3. ESR spectrum of  $\text{Mn}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  (toluene; 203 K).

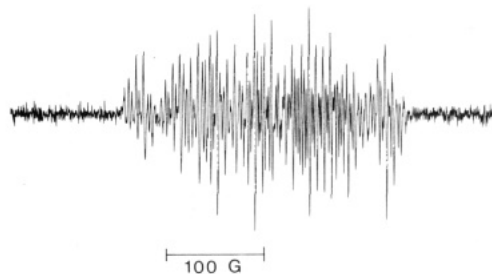


Figure 4. ESR spectrum of  $(\text{P}(\text{OPh})_3)\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$  (benzene; 293 K).

PyCa) radicals were too unstable to be observed with ESR without using a spin-trapping reagent.

The  $g$  factors derived for the observed radicals are rather close to the free electron value ( $g_e = 2.0023$ ) and different from the  $g$  factors reported by Kidd, Chen, and Brown<sup>9d</sup> and by Gross and Kaim<sup>23</sup> for Mn-centered radicals ( $g \approx 2.03$ ). This means that the electron resides at the  $\alpha$ -diimine ligand, and these radicals are best considered as the 16e radical anion complexes in which  $\text{Mn}^+$  or  $\text{Re}^+$  ( $d^6$ ) is surrounded by three carbonyl groups and a negatively charged  $\alpha$ -diimine ligand. Because of this and of the persistent character of  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^\bullet$ , adduct formation of these radicals with various ligands could be studied.

**ESR Spectra of the Adducts.** After photochemical formation of the radicals and optimization of the ESR signals, a small quantity of the nucleophiles was added to the solution in the ESR tube. The ESR spectrum changed immediately into the spectrum of a new paramagnetic species with larger coupling constants and more multiplets. For the reaction of phosphines, only  $\text{P}(\text{OPh})_3$  and  $\text{P}(\text{OMe})_3$  could be used since more basic ligands such as  $\text{P}(n\text{-Bu})_3$  gave no detectable adducts, probably due to secondary thermal substitution reactions. The spectra of these ad-

(22) Reinhold, J.; Benedix, R.; Birner, P.; Hennig, H. *Inorg. Chim. Acta* 1979, 33, 209.

(23) Gross, R.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* 1980, 24, 856.

Table II. ESR Parameters<sup>a</sup> for (L')Re(CO)<sub>3</sub>(*t*-Bu-DAB)

L'	solvent	T, K	a <sub>Re</sub>	a <sub>L'</sub> <sup>b</sup>	a <sub>N</sub> <sup>c</sup>	a <sub>H</sub> <sup>d</sup>	g
PPh <sub>3</sub>	benzene	293	35.61		7.26	4.65	2.0036
PPh <sub>3</sub>	benzene	293	39.73	39.73 <sup>e</sup>	7.40	4.45	2.0047
P(OPh) <sub>3</sub>	benzene	293	41.15	34.55	7.17	4.35	2.0074
P(OMe) <sub>3</sub>	benzene	293	39.98	35.78	7.20	4.48	2.0090
pyridine		293	31.12	4.91	6.52	no <sup>f</sup>	2.0030
pyridine	cyclohexane	343	31.80	5.31	6.32	no	2.0028

<sup>a</sup> Coupling constants in gauss ( $\pm 0.05$ ). <sup>b</sup> L' = <sup>31</sup>P ( $I = 1/2$ ) or L' = <sup>14</sup>N ( $I = 1$ ). <sup>c</sup> Imine nitrogen nuclei. <sup>d</sup> Imine hydrogen nuclei. <sup>e</sup> a<sub>Re</sub> and a<sub>L'</sub> could not be distinguished from each other. <sup>f</sup> no = not observed.

Table III. ESR Parameters<sup>a</sup> for Nitroxides (t-Bu)N(O')M'(CO)<sub>3</sub>L'

M'	$\alpha$ -diimine	a <sub>M'</sub>	a <sub>N</sub> (NO)	a <sub>N</sub> ( $\alpha$ -diimine)	g
Re	<i>p</i> -Tol-DAB	35.9 <sup>b</sup>	no <sup>c</sup>	no	2.0048
	<i>t</i> -Bu-DAB	34.86	14.01	no	2.0124
Re	<i>i</i> -Pr-PyCa	30.46	13.60	no	2.0087
Re	phen	27.40	13.59	no	2.0104
Re	bpy <sup>d</sup>	27.20	13.53	no	2.0112
Mn	<i>i</i> -Pr-PyCa	7.25	14.55	0.96	2.0098
Mn	phen	6.94	13.98	0.89	2.0102
Mn	bpy'	6.88	13.94	0.93	2.0105

<sup>a</sup> Coupling constants in gauss ( $\pm 0.05$ ) and measured in 5 mM *t*-Bu-NO/THF solutions at 293 K. <sup>b</sup> Very broad signals. <sup>c</sup> no = not observed. <sup>d</sup> bpy' = 4,4'-dimethyl-2,2'-bipyridine.

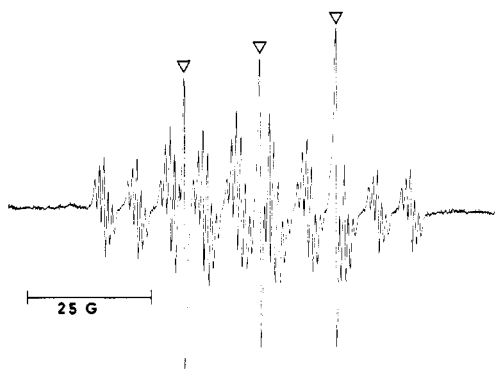


Figure 5. ESR spectrum of (t-Bu)N(O')Mn(CO)<sub>3</sub>(phen) (THF; 293 K) (▽ = signals due to (t-Bu)<sub>2</sub>NO\*).

ducts were analyzed by computer simulations, and hfs were found for one <sup>185,187</sup>Re nucleus, for two equivalent <sup>14</sup>N and <sup>1</sup>H nuclei, and for one <sup>31</sup>P nucleus (34.55 G for P(OPh)<sub>3</sub>; 35.78 G for P(OMe)<sub>3</sub>) or one <sup>14</sup>N nucleus (4.91 G for pyridine). A representative spectrum is shown in Figure 4, and the data are collected in Table II.

**ESR Spectra of Spin-Trapped Radicals.** Irradiation (see Experimental Section) at room temperature of THF solutions of (CO)<sub>3</sub>MM'(CO)<sub>3</sub>L or Ph<sub>3</sub>SnRe(CO)<sub>3</sub>L (M, M' = Mn, Re; L =  $\alpha$ -diimine) containing ca. 5 mM *t*-BuNO as the spin-trapping reagent resulted in the formation of the fairly persistent spin adducts (t-Bu-NO\*)(Mn(CO)<sub>3</sub>L) with the odd electron residing on  $\pi^*_{NO}$ . This is concluded from the close agreement between the values of a<sub>N</sub>(NO) derived from the ESR spectra of these adducts and those of other spin adducts.<sup>24</sup> A representative ESR spectrum is shown in Figure 5, and the ESR parameters are collected in Table III. Thus, by formation of the spin adducts with *t*-Bu-NO,<sup>13b,24</sup> the equilibria of Scheme I can be shifted to

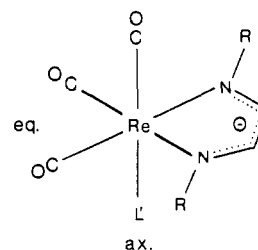


Figure 6. Proposed molecular geometry of the adducts (L')-Re(CO)<sub>3</sub>(*t*-Bu-DAB)\* (L' = PR<sub>3</sub> or pyridine).

the monomer side in the case of Mn(CO)<sub>3</sub>(*i*-Pr-PyCa)\* and Mn(CO)<sub>3</sub>(bpy)\*.

## Discussion

Before the ESR data of the radicals and their adducts are discussed, their electronic and molecular structures have to be established. All complexes XM'(CO)<sub>3</sub>L (X = Mn(CO)<sub>5</sub>, Re(CO)<sub>5</sub>, Co(CO)<sub>4</sub>, CpFe(CO)<sub>2</sub>, or Ph<sub>3</sub>Sn; M' = Mn, Re; L =  $\alpha$ -diimine) show the formation of the same radical in equilibrium with a dimeric species, which has been identified as the stable M'<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub> complex.<sup>19a,25,26</sup> The stability of the radical is mainly determined by the position of this equilibrium. This means that steric and electronic effects preventing the formation of the dimers have a stabilizing influence on the radical. The most important factor here is the size of the R substituent in the case of the R-DAB radical complexes, a bulky group such as *t*-Bu preventing the formation of the dimer. A similar stabilizing influence of bulky groups on radicals has been observed by Brown and co-workers for the Mn(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> radicals.<sup>9d-g</sup>

No proof for the composition of the radicals can be given since their concentrations are far too low for identification with spectroscopic techniques other than ESR. There is, however, substantial evidence from what has been said above, that we are dealing here with radicals of the type M'(CO)<sub>3</sub>L\*. The persistence of these radicals, which contrasts with the instability of the metal-centered M'(CO)<sub>5</sub> species,<sup>3,9a,b,g,12a</sup> points to an electronic configuration in which the electron resides in a low-energy, ligand-localized  $\pi^*$  orbital. Evidence for this electronic configuration comes from the characteristic features of the ESR spectra, such as line widths (not larger than 0.5 G) and lack of anisotropy in *g* and its value, which approaches the free electron value *g*<sub>e</sub> = 2.0023. Especially this close agreement between the *g* values of the radicals and *g*<sub>e</sub> points to a complex in which the electron is localized in the lower  $\pi^*$  orbital of the ligand L, which has only light atoms and therefore gives rise to only small spin-orbit coupling factors. Such a M'(CO)<sub>3</sub>L\* radical, with the electron predominantly on L, can be considered as a 16e species which will easily take up a solvent molecule. This coordinatively unsaturated character is evident from the tendency of these radicals to form adducts with nucleophilic ligands such as phosphines, pyridine, and *t*-Bu-NO. In the case of P(OPh)<sub>3</sub>, an adduct is formed that clearly shows <sup>31</sup>P coupling apart from the other hfs (see Table II). The question remains how the solvent molecule or nucleophile coordinates to the metal in the equatorial metal- $\alpha$ -diimine plane or in an axial position. For the corresponding quinone radicals (L')Re(CO)<sub>3</sub>Q\*, Creber and Wan<sup>13f</sup> have deduced from the IR spectra that L' is coordinated in an axial position. This conclusion was supported by the observation of large coupling constants *a*<sub>p</sub> for the PR<sub>3</sub>-substituted radicals,

(24) (a) Rehorek, D.; Hennig, H. *Can. J. Chem.* 1982, 60, 1565. (b) Hudson, A. H.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* 1974, 966. (c) Brenner, L. S.; Balch, A. L. *J. Organomet. Chem.* 1977, 134, 121.

(25) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1976, 98, 3931. (26) Kruck, T.; Höfler, M.; Noacke, M. *Chem. Ber.* 1966, 99, 1152.

since equatorial P atoms are expected to show much smaller coupling constants. Similar large  $a_p$  hfs have been observed for several other phosphine-substituted radical complexes<sup>13f,27,28</sup> and for the  $(PR_3)M'(CO)_3L^*$  radicals under study. Accordingly the structure shown in Figure 6 is proposed for these radicals.

The distribution of the spin in the lowest  $\pi^*$  orbital of L will of course depend on the atomic orbital coefficients of this orbital. Thus, in R-DAB this orbital is mainly localized at the coordinating nitrogen atoms, whereas the spin in the corresponding phenanthroline ligand will be much more delocalized over the ring system. This difference in spin distribution will in turn strongly influence the coupling constant of the metal (vide infra).

Adduct formation with the  $\pi$ -back-bonding ligands  $P(OMe)_3$  and  $P(OPh)_3$  causes a shift of electron density toward both these ligands and the metal. Again these effects are clearly reflected in the coupling constants,  $a_{Re}$  being larger for the phosphite adducts than for the solvated radical species. Adduct formation with *t*-Bu-NO causes a complete change of the ESR spectrum since the electron shifts to the very low-lying  $\pi^*$  orbital of NO.

**Coupling Constants.** The coupling constants give valuable information about the atomic orbital coefficients of the LUMO of the parent compounds.<sup>31</sup> From the data presented in Table I, several trends can be derived for the  $a_{Re}$  values of the  $Re(CO)_3L^*$  radicals. First of all,  $a_{Re}$  increases on going from L = phen via R-PyCa to R-DAB. This points to an increase of spin population at the coordinating nitrogen atoms, giving rise to an increase of the  $\sigma/\pi$  spin polarization.<sup>17a</sup> This increase of spin population at nitrogen on going from the phen to the R-DAB radical anion complex agrees with the more localized nature of the LUMO of the R-DAB ligand. It is also in accordance with the observed increase of metal to L  $\pi$ -back-bonding along this series in the neutral parent compounds.<sup>17b,19,20,22</sup> Second, the  $a_N$  values of the  $Re(CO)_3L^*$  radicals are higher than those of the reduced ligand  $L^*$ , which again points to a higher spin population at the nitrogen atoms.<sup>28,30</sup> There appears to be a close relationship between  $a_N$  and  $a_{Re}$  ( $a_{Re} = ca_N$ ) of the  $Re(CO)_3L^*$  radicals. Such a relationship has also recently been observed by Kaim and Kohlmann<sup>31</sup> for the radical anion complexes  $M(CO)_5L^*$  and  $M(CO)_4L^*$  ( $M = Cr, Mo, W$ ;  $L = N$ -heterocyclic ligands, e.g. tetrazine and azo-2,2'-bipyridine). Third, in the  $Re(CO)_3(R-DAB)^*$  radical complexes the electronic properties of the substituent R have a strong influence on the spin population at N. On going from  $Re(CO)_3(t-Bu-DAB)^*$  to  $Re(CO)_3(p-Tol-DAB)^*$   $a_N$  decreases by 2 G. In the latter radical the electron is partly delocalized to the *p*-Tol groups.

The influence of the metal on the electron density distribution in the radical anion is evident from a comparison of the coupling constants  $a_N$  and  $a_H$  of the radicals  $M'(CO)_3(t-Bu-DAB)^*$  ( $M' = Mn, Re$ ),  $RZn(t-Bu-DAB)^*$ , and  $R_2Al(t-Bu-DAB)^*$  ( $R = alkyl$ ). The values of  $a_N$  and  $a_H$  hardly differ for the Mn and Re radicals, but  $a_N$  is about 2.4 G higher and  $a_H$  (imine) is about 1 G lower for the Re than for the Zn and Al radicals.<sup>18,32,33</sup> These coupling

constants  $a_N$  and  $a_H$  can be used to calculate the electron densities at the N and H atoms of the ligand.<sup>39</sup> The remaining charge of the radical electron then resides on the imine carbon atoms. In this way the calculated electron density of the imine carbons appeared to be 0.2 for  $R'Zn(t-Bu-DAB)^*$ <sup>33</sup> but only 0.07 for the  $Re(CO)_3(t-Bu-DAB)^*$  radical. This difference in charge density may explain why C-C coupling reactions between the R-DAB ligands of the radicals have only been observed for the Zn radicals. For the corresponding  $Mn(CO)_3(t-Bu-DAB)^*$  radical complex, the hfs  $a_{Mn}$  (8.47 G) is much lower than  $a_{Re}$  for the corresponding Re complex as a result of the lower natural isotropic hfs of Mn.<sup>29</sup> The observed ratio of the coupling constants ( $a_{Re}/a_{Mn} = 4.1$ ) is in agreement with the one found by Wan et al. for  $M(CO)_4(o\text{-quinone})^*$  ( $M = Mn, Re$ ) ( $a_{Re}/a_{Mn} = 4.1$ )<sup>13a</sup> and  $M(CO)_4(BETS)^*$  ( $M = Mn, Re$ ; BETS = bis(ethoxythiocarbonyl) sulfide) ( $a_{Re}/a_{Mn} = 4.3$ ).<sup>34</sup> The adducts of the phosphites with  $Re(CO)_3(t-Bu-DAB)^*$  show an increase in the hfs  $a_{Re}$  of about 5 G with respect to the solvated radical anion complex (see Table II). This increase in  $a_{Re}$  and the concomitant decrease in  $a_N$ (imine) and  $a_H$ (imine) result from the stronger  $\pi$ -back-bonding abilities of these ligands with respect to the solvent molecules. For the adduct of pyridine the situation is reversed.

The hfs  $a_p$  and  $a_N$ (pyridine) are caused by  $\sigma/\pi$  hyperconjugation between the electron in the ligand  $\pi^*$  orbital and the electron in the axial Re-P bond. An increase in  $a_p$  always induces an increase in  $a_{Re}$ , which is in agreement with data from the literature.<sup>13,34,35</sup> The change of spin population upon formation of the adduct of *t*-Bu-NO with  $Mn(CO)_3(t-Bu-DAB)$  is evident from a large decrease in  $a_N$  of the ligand L. In these nitroxides a decrease in  $a_M$  on going from R-DAB via R-PyCa to phen and bpy is accompanied by a decrease in  $a_N$ (NO). This change indicates an increase in electron-donating character of the  $M'(CO)_3L$  fragment in the same order. The bpy' and phen ligands are much stronger  $\sigma$  donors and weaker  $\pi$  acceptors than R-DAB, thus creating more electron density at the metal centers.<sup>22</sup> As a result the electron becomes more localized at the oxygen atom. Also for these complexes  $a_{Re}/a_{Mn}$  has a value of 4.0.

***g* Values.** The *g* values of radical (ion) complexes, the "chemical shifts", are also a very useful source of information about the electronic structure of such complexes.<sup>13-17,27,28,30-33,36</sup> The *g* values are in contrast to the hfs values, solvent and temperature dependent. In general, small deviations of *g* from the free electron value  $g_e$  may be attributed to the admixture of higher excited states to the (doublet) radical ground state via the relation<sup>29</sup>

$$g = g_e \pm \xi/\Delta$$

where  $\xi$  is the spin-orbit coupling factor and  $\Delta$  the energy separation between the singly occupied orbital (SOMO;  $E_o$ ) and the orbital ( $E_n$ ) with which it can mix by spin-orbit coupling. For all the  $M'(CO)_3L^*$  ( $M' = Mn, Re$ ;  $L = \alpha$ -diimine) radical complexes the *g* values are higher than  $g_e$  but are not very different from the *g* values reported for the free ligand anions (*i*-Pr-DAB $\cdot K^+$ ,  $g = 2.0034$ ;<sup>32</sup> bpy $\cdot K^+$ ,  $g = 2.0026$ ),<sup>30</sup> once again an argument that the odd electron may be considered as ligand localized in  $M'(CO)_3L^*$ .

(33) Van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, *250*, 49 and references therein.

(34) McGimpsey, W. G.; Depew, M. C.; Wan, J. K. S. *Organometallics* **1984**, *3*, 1684.

(35) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498.

(36) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171.

(27) (a) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365. (b) Ernst, S.; Kaim, W. *J. Chem. Phys.* **1986**, *90*, 5010.

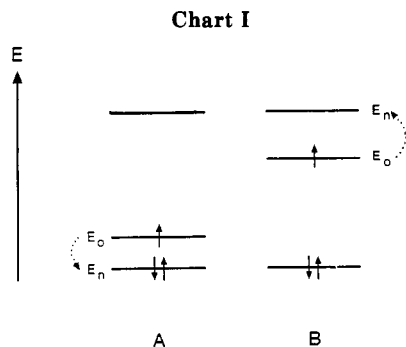
(28) tom Dieck, H.; Franz, K.-D.; Hohmann, F. *Chem. Ber.* **1975**, *108*, 163.

(29) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 136.

(30) (a) Kaim, W. *J. Am. Chem. Soc.* **1982**, *104*, 3833. (b) Kaizu, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 470.

(31) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442.

(32) tom Dieck, H.; K hl, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 324.



In the series of  $\text{Re}(\text{CO})_3\text{L}^*$  radicals the isotropic  $g$  values decrease in the order  $\text{L} = i\text{-Pr-DAB}$  (2.0059),  $i\text{-Pr-PyCa}$  (2.0051), and  $\text{phen}$  (2.0040). At the same time  $a_{\text{Re}}$  decreases from 38.41 G to 28.14 and 20.88 G. This reduction of spin population at the rhenium and coordinating nitrogen atoms, reflected in the decreases in  $a_{\text{Re}}$  and  $a_{\text{N}}$ , will be accompanied by a reduction of the contribution of the spin-orbit coupling  $\xi_{\text{Re}}$  and also of the deviation of  $g$  from  $g_e$ .

It is remarkable that the  $g$  values of  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^*$  and  $\text{Mn}(\text{CO})_3(t\text{-Bu-DAB})^*$  hardly differ from each other, although  $\xi_{\text{Mn}}$  ( $239\text{ cm}^{-1}$ )<sup>29</sup> is about 10 times lower than  $\xi_{\text{Re}}$  ( $2285\text{ cm}^{-1}$ ).<sup>29</sup> For most radical anion complexes with group 6 metal carbonyls, e.g.,  $\text{M}(\text{CO})_4\text{L}^{\cdot-}$  ( $17\text{b}, 28, 32$ ) ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{L} = \alpha\text{-diimine}$ ) or  $(\text{CO})_5\text{M-L}^{\cdot-}\text{M}(\text{CO})_5$  ( $\text{L} = \mu\text{-1,4-diazines}$ ),<sup>27, 31, 35</sup>  $g$  increases in the order  $g(\text{ligand}) \approx g(\text{Cr complex}) < g(\text{Mo complex}) \ll g(\text{W complex})$ . The much larger value of  $g$  for the tungsten complex is due to the high spin-orbit coupling factor  $\xi_{\text{M}}$ .<sup>29</sup> Only for group 6 metal carbonyl complexes with the binucleating ligand 2,2'-bipyrimidine this order appeared to be reversed.<sup>27</sup> This effect has been explained by a change in the sign of  $\Delta$  in  $g = g_e \pm \xi/\Delta$  due to a mixing between the SOMO and a close-lying empty orbital (Chart IB) instead of a mixing between the SOMO and a doubly occupied orbital (Chart IA). This model was also used to explain the low  $g$  values observed for the  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}^{\cdot-}$  radical anion complexes (e.g.,  $\text{L} = \text{pyrazine}$ ).<sup>35</sup> Although these effects are most pronounced for paramagnetic transition-metal ions such as  $d^9$  systems (case A,  $g > g_e$ ) or  $d^1$  systems (case B,  $g < g_e$ )<sup>29</sup> where the difference between the d levels is much smaller than the gap between d orbitals and the next filled or unfilled s or p levels, this approach has also successfully been employed for delocalized organometallic radical complexes.<sup>35</sup>

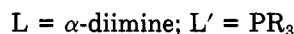
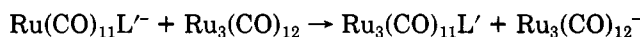
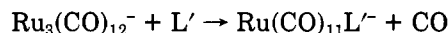
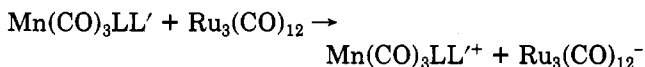
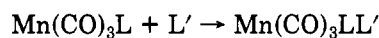
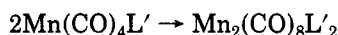
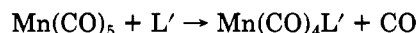
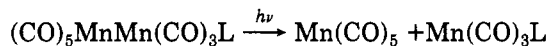
Thus, the small change of  $g$  on going from  $\text{Mn}(\text{CO})_3(t\text{-Bu-DAB})^*$  to  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^*$ , despite the large increase of  $\xi$ , may be attributed to a change from system A (Mn) to system B (Re). It has also to be mentioned that these "reversed shifts" have been observed before for the  $\text{M}(\text{CO})_4(o\text{-quinone})^*$  and  $\text{M}(\text{CO})_4(\text{BETS})^*$  complexes ( $\text{M} = \text{Mn}, \text{Re}$ ) by Forster et al.<sup>13a</sup> and McGimpsey et al.<sup>34</sup> but these authors did not pay any attention to this effect.

The  $g$  values of the nitroxide spin adducts  $(t\text{-Bu})\text{N}(\text{O}^{\cdot})\text{M}'(\text{CO})_3\text{L}$  (Table III) are higher than  $g_e$ , but these deviations are comparable to those observed for  $(t\text{-Bu})_2\text{NO}^*$  (2.006 06)<sup>37</sup> and  $(i\text{-Bu})_2\text{NO}^*$  (2.005 85).<sup>38</sup> These "high" values are caused by the  $\xi$  value of oxygen.<sup>39</sup>

The  $g$  values of the  $\text{PR}_3$  adducts of the  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^*$  radical species are higher than that of the solvated

radical  $(\text{S})\text{Re}(\text{CO})_3(t\text{-Bu-DAB})^*$ , a result which is expected since an increase in  $a_{\text{Re}}$  induces an increase in  $\xi_{\text{Re}}$  in  $\Delta g = \xi/\Delta$ .

**Chemical Aspects.** The above ESR spectra show that the  $\text{M}'(\text{CO})_3\text{L}$  ( $\text{M}' = \text{Mn}, \text{Re}$ ;  $\text{L} = \alpha\text{-diimine}$ ) radicals, which can easily be obtained by visible excitation of a series of complexes  $\text{XM}'(\text{CO})_3\text{L}$  ( $\text{X} = \text{Mn}(\text{CO})_5, \text{Re}(\text{CO})_5, \text{Co}(\text{CO})_4, \text{CpFe}(\text{CO})_2, \text{CpMo}(\text{CO})_3, \text{SnPh}_3$ ), have their unpaired electron residing on the ligand L. They can therefore best be described as  $d^6\text{M}'^+(\text{CO})_3\text{L}^{\cdot-}$  radicals with a 16e configuration for the metal ion. In this respect they differ from the metal-localized 17e radicals  $\text{Mn}(\text{CO})_3(\text{PR}_3)_2$ , which have been characterized by Brown and co-workers.<sup>9d</sup> Both types of radicals have, however, in common that they are most stable when they possess bulky substituents inhibiting dimerization. Because of their 16e configuration, the  $\text{M}'(\text{CO})_3\text{L}$  radicals readily pick up a nucleophile to give 18e adducts that could be detected and characterized with ESR for several N- and P-donor ligands. These adducts are chemically important species since they are highly reducing agents that can easily start catalytic disproportionation<sup>20, 41</sup> and electron-transfer-catalyzed (ETC) substitution<sup>2, 3, 6, 41</sup> reactions. An example of the latter type of reaction is the substitution of CO in  $\text{Ru}_3(\text{CO})_{12}$  by  $\text{PR}_3$ .<sup>41</sup> This reaction proceeds catalytically when it is triggered by light in the presence of a small amount of  $(\text{CO})_5\text{Mn-Mn}(\text{CO})_3\text{L}$ . The following mechanism has been proposed:



These disproportionation and substitution reactions are analogous to those induced by the 19e species derived from the 17e radicals  $\text{Mn}(\text{CO})_5$ ,  $\text{CpMo}(\text{CO})_3$ , and  $\text{CpFe}(\text{CO})_2$ , which have been studied in detail by Tyler and co-workers.<sup>3, 6, 7</sup> In contrast to the above 16e and 18e radicals, however, these 19e species (e.g.,  $\text{Mn}(\text{CO})_3(\text{N-donor})_3$ ) are very short-lived and have not been detected so far.

### Experimental Section

The complexes  $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$  and  $\text{Ph}_3\text{SnM}'(\text{CO})_3(\alpha\text{-diimine})$  ( $\text{M}, \text{M}' = \text{Mn}, \text{Re}$ ;  $\alpha\text{-diimine} = \text{bpy}, \text{phen}, \text{R-PyCa}$ , or  $\text{R-DAB}$ ) were synthesized according to literature methods.<sup>13, 19, 40</sup> All spectroscopic samples were dissolved in freshly distilled and deoxygenated solvents and prepared with standard inert-gas techniques. Special care was taken to exclude all light during the manipulations of the samples.

ESR spectra were measured on a Bruker ER-200D-MR X-band spectrometer with 100-kHz modulation and temperature accessory. Coupling constants were obtained by computer simulations.

For the photolysis experiments an Oriel mercury arc source equipped with an Osram HBO 200-W mercury lamp was used

(37) Kawamura, T.; Matsunami, S.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* 1967, 40, 1111.

(38) Baird, J. C. *J. Chem. Phys.* 1962, 37, 1879.

(39) Bersohn, M.; Baird, J. C. *An Introduction to Electron Paramagnetic Resonance*; W. A. Benjamin: New York, 1966.

(40) (a) Luong, J. C.; Faltyrek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* 1979, 101, 1597. (b) *Ibid.* 1980, 102, 7892.

(41) van der Graaf, T.; Stufkens, D. J.; Oskam, A., unpublished results.

together with appropriate cut of light filters ( $\lambda \geq 320$  nm). The beam was focused on the center of the microwave cavity.

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**Registry No.**  $\text{Re}(\text{CO})_3(i\text{-Pr-DAB})'$ , 113110-69-3;  $\text{Re}(\text{CO})_3(t\text{-Bu-DAB})'$ , 113110-70-6;  $\text{Re}(\text{CO})_3(p\text{-Tol-DAB})'$ , 113110-71-7;  $\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})'$ , 113110-72-8;  $\text{Re}(\text{CO})_3(\text{phen})'$ , 113110-73-9;

$\text{Mn}(\text{CO})_3(t\text{-Bu-DAB})'$ , 96455-75-3;  $(\text{PPh}_3)\text{Re}(\text{CO})_3(t\text{-Bu-DAB})$ , 113110-74-0;  $(\text{P}(\text{OPh})_3)\text{Re}(\text{CO})_3(t\text{-Bu-DAB})$ , 113110-75-1;  $(\text{P}(\text{OMe})_3)\text{Re}(\text{CO})_3(t\text{-Bu-DAB})$ , 113110-76-2;  $(\text{Pyridine})\text{Re}(\text{CO})_3(t\text{-Bu-DAB})$ , 113110-77-3;  $(t\text{-Bu})\text{N}(\text{O}')\text{Re}(\text{CO})_3(p\text{-Tol-DAB})$ , 113110-78-4;  $(t\text{-Bu})\text{N}(\text{O}')\text{Re}(\text{CO})_3(t\text{-Bu-DAB})$ , 113110-79-5;  $(t\text{-Bu})\text{N}(\text{O}')\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})$ , 113110-80-8;  $(t\text{-Bu})\text{N}(\text{O}')\text{Re}(\text{CO})_3(\text{phen})$ , 113132-25-5;  $(t\text{-Bu})\text{N}(\text{O}')\text{Re}(\text{CO})_3(\text{bpy}')$ , 113110-81-9;  $(t\text{-Bu})\text{N}(\text{O}')\text{Mn}(\text{CO})_3(i\text{-Pr-PyCa})$ , 113110-82-0;  $(t\text{-Bu})\text{N}(\text{O}')\text{Mn}(\text{CO})_3(\text{phen})$ , 113132-26-6;  $(t\text{-Bu})\text{N}(\text{O}')\text{Mn}(\text{CO})_3(\text{bpy}')$ , 113132-27-7.

## Novel Ylide-Type Rhodium Complexes Containing a Six-Membered $\text{RhCH}_2\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2$ Ring<sup>1</sup>

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The chelate rhodium(I) complexes  $\text{C}_5\text{H}_3\text{Rh}[1,2\text{-C}_2\text{H}_4(\text{PR}_2)_2]$  (2, R = Ph; 3, R = Me) have been prepared from  $[\text{L}_2\text{RhCl}]_2$  (L =  $\text{C}_2\text{H}_4$ ,  $\text{C}_8\text{H}_{14}$ ), the diphosphine (dppe or dmpe), and  $\text{MC}_5\text{H}_5$  (M = Na, Tl). Compounds 2 and 3 react with  $\text{CH}_2\text{I}_2$  by oxidative addition to give the (iodomethyl)rhodium(III) compounds  $[\text{C}_5\text{H}_5\text{RhCH}_2\text{I}(1,2\text{-C}_2\text{H}_4(\text{PR}_2)_2)]\text{I}$  (4a, 5a) which have been converted by reaction with  $\text{NH}_4\text{PF}_6$  to the more stable  $\text{PF}_6^-$  salts 4b and 5b. Whereas 4b is completely inert in nitromethane solution, 5b on addition of  $\text{NEt}_3$  isomerizes quantitatively to give the metallaheterocycle  $[\text{C}_5\text{H}_5(\text{I})\text{RhCH}_2\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2]\text{PF}_6$  (7).

The corresponding dicationic derivative  $[\text{C}_5\text{H}_5(\text{PMe}_3)\text{RhCH}_2\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2](\text{PF}_6)_2$  (8) is obtained by ligand exchange. The molecular structure of 7 has been determined by X-ray analysis. Compound 7 crystallizes in the space group  $P2_1/n$  with  $a = 848.2$  (2) pm,  $b = 1489.5$  (4) pm,  $c = 1594.6$  (4) pm, and  $\beta = 103.17$  (2)°. The six-membered ring in the cation of 7 adopts a chair conformation. Complex 7 has also been prepared from  $\text{C}_5\text{H}_5\text{RhCH}_2\text{I}[\text{P}(\text{OMe})_3]\text{I}$  and dmpe in the presence of  $\text{NH}_4\text{PF}_6$ . In contrast, the analogous (iodomethyl)rhodium compound  $\text{C}_5\text{H}_5\text{RhCH}_2\text{I}(\text{PMe}_3)\text{I}$  reacts with dmpe (and  $\text{NH}_4\text{PF}_6$ ) to produce a dinuclear-bridged species which presumably has the composition  $\{[\text{C}_5\text{H}_5(\text{PMe}_3)(\text{I})\text{Rh}]_2(\mu\text{-CH}_2\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2\text{CH}_2)\}(\text{PF}_6)_2$  (9). The cobalt complexes  $\text{C}_5\text{H}_5\text{Co}(\text{dmpe})$  (12),  $[\text{C}_5\text{H}_5(\text{CO})\text{Co}]_2(\mu\text{-dmpe})$  (13),  $\text{C}_5\text{H}_5\text{Co}(\text{CO})(\eta^1\text{-dppm})$  (14), and  $[\text{C}_5\text{H}_5\text{CoCOCH}_3(\eta^2\text{-dppm})]\text{I}$  (15) also have been prepared by using either  $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$  or  $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$  as starting material.

### Introduction

We have recently shown that cyclopentadienylcobalt and -rhodium complexes of general composition  $\text{C}_5\text{H}_5\text{MLL}'$  (where L =  $\text{PR}_3$  and L' =  $\text{PR}_3$ ,  $\text{P}(\text{OR})_3$ , CO,  $\text{C}_2\text{H}_4$ , etc.) are metal bases and react not only with Brønsted acids and alkyl iodides but also with  $\text{CH}_2\text{I}_2$  and other dihalomethanes by oxidative addition.<sup>2</sup> The two types of products obtained,  $[\text{C}_5\text{H}_5\text{MCH}_2\text{X}(\text{L})\text{L}']\text{X}$  and  $[\text{C}_5\text{H}_5\text{MCH}_2\text{X}(\text{L})\text{X}]$ , contain a carbenoid-metal fragment that proved to be very reactive toward nucleophiles. Using the neutral (iodomethyl)rhodium complex 1 as an example, the results summarized in Scheme I illustrate that the course of the nucleophilic attack on the C-X bond of the  $\text{RhCH}_2\text{X}$  unit is strongly dependent on the nature of the nucleophile used. Whereas with pyridine, phosphines, and phosphites cationic ylide rhodium compounds are formed,<sup>3</sup> treatment of 1 with  $\text{SH}^-$ ,  $\text{SeH}^-$ , or  $\text{TeH}^-$  gives, probably via a  $\text{RhCH}_2\text{EH}$  intermediate, the corresponding thio-, seleno-, and telluroformaldehyde complexes.<sup>4</sup> The hydroxide ion,

however, in presence of a phase-transfer catalyst, reacts with 1 in a different way, producing the isomer  $[\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2\text{PMe}_3)\text{I}_2]$  which is not accessible by other routes.<sup>3,4</sup>

It was this unexpected isomerization that led us to investigate the mechanism and scope of this reaction in more detail. During these studies we observed that also the ionic carbenoid complexes  $[\text{C}_5\text{H}_5\text{RhCH}_2\text{I}(\text{PMe}_3)_2]\text{PF}_6$  and  $[\text{C}_5\text{H}_5\text{RhCH}_2\text{I}(\text{PR}_3)\text{L}]\text{PF}_6$  isomerize thermally or in the presence of  $\text{NEt}_3$  to produce ylide rhodium compounds of composition  $[\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2\text{PMe}_3)(\text{PMe}_3)\text{I}]\text{PF}_6$  and  $[\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2\text{PR}_3)(\text{L})\text{I}]\text{PF}_6$ .<sup>5</sup> Kinetic studies for  $\text{PR}_3 = \text{PMe}_3$  and L =  $\text{P}(\text{OMe})_3$  revealed a distinct dependence of the rate of isomerization on the  $\text{NEt}_3$  concentration and suggested an intramolecular exchange mechanism similar to that known for dyotropic rearrangements. The question that seemed to be most interesting to us, however, was whether carbenoid complexes having a chelate ligand coordinated to the metal would behave similarly and would thus open a synthetic route to cyclic ylide-type transition-metal complexes. It is worth mentioning that more recently Weber et al., using a different approach to this target, prepared five- and six-membered ylide-chelate chromium compounds by the reaction of  $\text{Cr}(\text{CO})_5[\text{CH}_2\text{S}(\text{O})\text{Me}_2]$  with  $\text{CH}_2(\text{ER}_2)_2$  and  $1,2\text{-C}_2\text{H}_4(\text{ER}_2)_2$  (E = P, As), respectively.<sup>6</sup> A short communication describing some

(1) Part 63 of the series "Metal Basicity". For part 62, see: Dziallas, M.; Höhn, A.; Werner, H. *J. Organomet. Chem.* 1987, 330, 207.

(2) Werner, H. *Angew. Chem.* 1983, 95, 932; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 927.

(3) (a) Werner, H.; Feser, R.; Paul, W.; Hofmann, L. *J. Organomet. Chem.* 1981, 219, C29. (b) Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* 1985, 118, 261.

(4) (a) Paul, W.; Werner, H. *Angew. Chem.* 1983, 95, 333; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 316; *Angew. Chem. Suppl.* 1983, 396. (b) Werner, H.; Paul, W.; Knaup, W.; Wolf, J.; Müller, G., manuscript to be submitted.

(5) Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* 1985, 281, 317.