Binuclear Metal Carbonyl R-DAB Complexes.[1] Synthesis and Spectroscopic Properties of Novel Heterodinuclear α-Diimine (R-DAB and R-Pyca) Complexes, Containing an Asymmetric Bridging Hydride. Molecular Structure of $[(\mu\text{-H})\mathrm{FeMn(CO)_6(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}\mathit{t}\text{-}Bu)}]$

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Reaction of [HFe(CO$_4$]$^-$ with [M(CO)$_3$(α-diimine)Br] (M = Mn, α-diimine = R-Pyca,[2a] R = *i*-Pr, *t*-Bu; M = Re, α-diimine = *i*-Pr-Pyca, or R-DAB,[2b] R = *i*-Pr, c-Hex, or *i*-Pr-DAB{H,CH$_3$}) at 40 °C in THF solution yields the heterodinuclear hydride species [(μ-H)FeM(CO)$_6$(α-diimine)]. The α-diimine ligand is σ-N,σ-N′ coordinated to M and η^2-C=N′ coordinated to Fe, thus donating six electrons to the metal carbonyl core. This bonding mode, which is well established for the R-DAB ligand but novel with respect to the R-Pyca ligand, is confirmed by an X-ray crystal structure determination of [(μ-H)FeMn(CO)$_6$(*t*-Bu-Pyca)]. Crystals of $C_{16}H_{15}FeMnN_2O_6$ are orthorhombic: space group $P2_12_12_1$ and cell constants *a* = 8.643 (6) Å, *b* = 14.143 (5) Å, *c* = 15.120 (5) Å, and *Z* = 4. A total of 4027 reflections have been used in the refinement, resulting in a final *R* value of 0.022. The most interesting feature of the structure is the asymmetrically bridging H(100) atom. For a bridging hydride the Fe–H(100) distance is rather short (1.61 (2) Å), while the Mn–H(100) is normal (1.73 (2) Å). The Mn–H(100)–Fe angle is 110 (1)°. The Fe–Mn distance of 2.7465 (3) Å is indicative of a Mn–Fe single bond. All six carbonyls are terminally bonded, three to Fe and three to Mn, with normal bond lengths and angles and with an eclipsed conformation. The *t*-Bu-Pyca ligand is bonded via the two N atoms to Mn with about equal bond lengths: Mn–N(1) = 2.060 (2) and Mn–N(2) = 2.051 (2) Å. Besides, the aliphatic imine part is also η^2-C=N coordinated to Fe with bond lengths: Fe–N(2) = 1.995 (1) and Fe–C(7) = 2.045 (1) Å. The α-diimine part of the ligand is not strictly planar with a torsion angle between the pyridylic N(1)=C(7) and aliphatic N(2)=C(8) bonds of 15.5 (2)°. The complexes have been further characterized by ^{1}H NMR, ^{13}C NMR, IR, and FD mass spectroscopy. These techniques indicate similar geometries in solution and in the solid state. The ^{1}H NMR spectra show the asymmetric bridging proton H(100) to resonate at ca. −16 ppm. When [HFe(CO)$_4$]$^-$ is reacted with [Re(CO)$_3$(*i*-Pr-DAB{H,CH$_3$})Br] of the two expected isomers, the one with the C(H)=N part being η^2-bonded is formed exclusively. When $[\mathrm{Fe}\underline{\mathrm{Re(CO)_6\{(\mathit{i}\text{-}Pr)NC(H)C}}\mathrm{(H)N(H)(\mathit{i}\text{-}Pr)\}}]$, containing an η^3-bonded 1-azaallylic moiety, is heated in toluene at 80 °C, it reacts via a first-order reaction (^{1}H NMR) to yield the isomeric hydride [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB)] almost quantitatively (FT-IR). A possible reaction mechanism is discussed.

Introduction

Part of the study in our research laboratory concerns the synthesis and chemistry of polynuclear carbonyls, containing the aliphatic α-diimine ligand R-DAB (R-DAB = 1,4-disubstituted 1,4-diaza-1,3-butadiene, RN=CHCH=NR)[2b] bonded to different metals at the same time.[1a-g] A neat possibility of synthesizing heterodinuclear R-DAB complexes is the reaction of carbonyl metalates with R-DAB containing metal halides.[1a,c] One of the reactions investigated, involved the interaction of [HFe(CO)$_4$]$^-$ with [Mn(CO)$_3$(R-DAB)Br] complexes. It was found that in these reactions the heterodinuclear complex $[\mathrm{Fe}\underline{\mathrm{Mn(CO)_6\{RNC(H)C}}\mathrm{(H)N(H)R\}}]$ was formed.[1a] During the reaction one hydrogen atom is transferred from the iron anion reagent to an imine N atom of the R-DAB ligand, thus reducing the neutral α-diimine to the monoanionic 3-(R-amino)-1-R-azaallylic moiety. Reaction of [Mn(CO)$_3$(*p*-tol-DAB)Br] with excess [HFe(CO)$_4$]$^-$ yields [(μ-H)FeMn(CO)$_6${μ,μ′-N(*p*-tol)CH$_2$CH$_2$N(*p*-tol)}] during which reaction the *p*-tol-DAB ligand is fully reduced to the dianionic 1,2-bis(*p*-tolylamino)ethane fragment as a result of the formation of two new C(ligand)–H bonds.[1g]

Because both conversion types are not to be expected for the α-diimine ligand R-Pyca[2a] (R-Pyca = C$_5$H$_4$N-2-CH=NR), one C=N double bond being resonance stabilized, we also investigated the reaction of [M(CO)$_3$(R-Pyca)Br] (M = Mn, Re) with [HFe(CO)$_4$]$^-$. Indeed, this time a heterodinuclear species was obtained with the R-

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[1] Part 12: for earlier parts see references 1a–f. (a) Keijsper, J.; Mul, J.; van Koten, G.; Vrieze, K.; Ubbels, H. C.; Stam, C. H. *Organometallics* **1984**, *3*, 1732. (b) Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Abbel, G.; Stam, C. H. *Inorg. Chem.*, accepted for publication. (c) Staal, L. H.; Keijsper, J.; van Koten, G.; Vrieze, K.; Cras, J. A.; Bosman, W. P. *Inorg. Chem.* **1981**, *20*, 555. (d) Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. *Inorg. Chem.* **1980**, *19*, 3343. (e) Staal, L. H.; Polm, L. H.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3590. (f) Staal, L. H.; van Koten, G.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 1830. (g) Keijsper, J.; Grimberg, P.; Vrieze, K.; Stam, C. H., in press.

[2] (a) Throughout this paper the pyridine-2-carbaldimines C$_5$H$_4$N-2-C(H)=NR are abbreviated as R-Pyca. (b) R-DAB stands for RN=C(H)C(H)=NR, while RN=C(R$_1$)C(R$_2$)=NR is abbreviated as R-DAB{R$_1$,R$_2$}. See, e.g.: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

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Pyca ligand still being a neutral α-diimine and with the hydride still bonded to the metal carbonyl core. This paper reports and discusses the synthesis and spectroscopic properties of these species and some R-DAB analogues, obtained from the reaction of $[\mathrm{Re(CO)_3(R\text{-}DAB)Br}]$ with $[\mathrm{HFe(CO)_4}]^-$.

Experimental Section

Materials and Apparatus. NMR spectra were obtained on a Varian T60 and a Bruker WM250 spectrometer (^{1}H) and on a Bruker WP80 apparatus (^{13}C). IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer; FT-IR spectra were obtained on a Nicolet 7199B FT-IR interferometer (liquid-nitrogen-cooled Hg, Cd, Te detector; 32 scans, resolution = 0.5 cm^{-1}) field desorption (FD) mass spectra were obtained with a Varian MAT 711 double-focusing mass spectrometer with a combined EI/FD/FI/ ion source and coupled to a spectro system MAT 100 data acquisition unit. Tungsten wire (10 μm) FD emitters containing carbon microneedles (average length = 30 μm) were used. The samples were dissolved in toluene or ether and loaded onto the emitter with the dipping technique. An emitter current between 0 and 10 mA was used to desorb the samples, the ion source temperature being 70 °C.[3] Elemental analyses were carried out by the section Elemental Analyses of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands.

The R-DAB$\{R_1,R_2\}$ ligands ($\mathrm{RN{=}C(R_1)C(R_2){=}NR}$; DAB = 1,4-diaza-1,3-butadiene)[2b] and the R-Pyca[2a] ligands ($\mathrm{RN{=}C(H)\text{-}2\text{-}C_5H_4N}$; Pyca = N-substituted pyridine-2-carbaldimine[2]) have been prepared via the condensation reactions of methylglyoxal[4] or pyridine-2-carbaldehyde,[5] respectively, with the appropriate primary amines. $[\mathrm{M(CO)_5Br}]$ (M = Mn, Re), $[\mathrm{M(CO)_3(R\text{-}DAB\{R_1,R_2\})Br}]$, and $[\mathrm{M(CO)_3(R\text{-}Pyca)Br}]$ have been prepared by procedures analogous to those in the literature.[6] A THF solution of $\mathrm{Na[HFe(CO)_4]}$ was prepared according to a modified literature procedure.[1a,7]

Synthesis of $[(\mu\text{-H})\mathrm{FeM(CO)_6}(\alpha\text{-diimine})]$ (M = Mn, α-diimine = R-Pyca,[2a] R = *i*-Pr, *t*-Bu; M = Re, α-diimine = *i*-Pr-Pyca or R-DAB,[2b] R = *i*-Pr, c-Hex, or *i*-Pr-DAB{H,CH$_3$}). A THF solution of $\mathrm{Na[HFe(CO)_4]}$ (prepared from 5.2 mmol of $\mathrm{Fe(CO)_5}$)[1a,7] was added to 3 mmol of $[\mathrm{M(CO)_3}(\alpha\text{-diimine})\mathrm{Br}]$ and the resulting solution stirred for 16 h at 40 °C. After filtration the filtrate was concentrated in vacuo, leaving a residue which was purified by column chromatography (silica; eluent ether/hexane = 1/5). Crystallization from pentane at −80 °C yielded yellow (M = Re) or orange/yellow (M = Mn) crystals in 40% (α-diimine = R-DAB$\{R_1,R_2\}$) or 80% (α-diimine = R-Pyca) yield. The crystals were identified as $[(\mu\text{-H})\mathrm{FeM(CO)_6}(\alpha\text{-diimine})]$ by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and FD mass spectroscopy (Tables IV–VI) and by an X-ray structure determination of $[(\mu\text{-H})\mathrm{FeMn(CO)_6}(t\text{-Bu-Pyca})]$. $[(\mu\text{-H})\mathrm{FeMn(CO)_6}(p\text{-tol-DAB})]$ was prepared similarly but it could only be isolated in less than 5% yield.

After the reaction of $[\mathrm{Re(CO)_3}(i\text{-Pr-DAB})\mathrm{Br}]$ with $[\mathrm{HFe(CO)_4}]^-$, elution of the reaction mixture with hexane/ether (1/1) yielded a yellow fraction, containing an isomeric mixed-metal 3-amino-1-azaallylic derivative, $[\mathrm{Fe}\underline{\mathrm{Re(CO)_6}\{(i\text{-Pr})\overline{\mathrm{NC(H)C}}\mathrm{(H)N}}\mathrm{(H)(i\text{-}Pr)}\}]$ (vide infra), which could be isolated as reported in the literature.[1a]

H Migration from Ligand to the Bimetallic Unit. When $[\mathrm{Fe}\underline{\mathrm{Re(CO)_6}\{(i\text{-Pr})\overline{\mathrm{NC(H)C}}\mathrm{(H)N}}\mathrm{(H)}(i\text{-Pr})\}]$, whose synthesis is described elsewhere,[1a] was heated at 80 °C in toluene, it reacted to yield isomeric $[(\mu\text{-H})\mathrm{FeRe(CO)_6}(i\text{-Pr-DAB})]$. The yield in solution was nearly quantitatively (as evidenced by ^{1}H NMR and FT-IR spectroscopy). Workup procedures were the same as described above. The reaction was followed with FT-IR spectroscopy by taking samples (by syringe) every 30 min and with ^{1}H NMR spectroscopy by warming a NMR tube, containing a toluene-d_8 solution of the starting complex, and taking spectra about every 30 min.

Table I. Crystal Data and Structure Determination Parameters

(a) Crystal Data

formula	$\mathrm{C_{16}H_{15}FeMnN_2O_6}$
mol wt	442.1
cryst system	orthorhombic
space group	$P2_12_12_1$
a, Å	8.643(6)
b, Å	14.143(5)
c, Å	15.120(5)
U, Å^3	1848(1) Å^3
Z	4
D(measd), g cm^{-3}	1.61
D(calcd), g cm^{-3}	1.589
F(000)	896
μ(Mo Kα), cm^{-1}	14.22
cryst size, mm	0.18 × 0.65 × 0.75
no. of grid points for abs correctn	8 × 8 × 6 = 384
min and max transmissn	0.466 and 0.784

(b) Data Collection

temp, K	295
$\theta_{\min}$ and $\theta_{\max}$, deg	1.35 and 27.5
radiatn	Mo Kα (Zr filtered); λ = 0.710 69 Å
w/2θ scan	$0.55 + 0.35 \tan\theta$
reference reflctns	400, 020, 004 (σ = 2%)
total data	9156
total unique	4242
obsd data	4029 ($I > 2.5\sigma(I)$)
total exposure time, h	150

(c) Refinement

no. of refined parameters	295
final $R_F = \Sigma(F_o - \lvert F_c\rvert)/\Sigma F_o$	0.0218
$R_{wF} = [\Sigma(F_o - \lvert F_c\rvert)^2/\Sigma F_o^2]^{1/2}$	0.0268
no. of reflctns	4027

Crystal Structure Determination of $[(\mu\text{-H})\mathrm{FeMn(CO)_6}(t\text{-Bu-Pyca})]$ (Hydridohexacarbonyl(*N-tert*-butylpyridine-2-carbaldimine)ironmanganese; $\mathrm{C_{16}H_{15}FeMnN_2O_6}$). The crystal data and structure determination parameters are summarized in Table I. The cell constants and their esd's were obtained from the setting of eight reflections. The intensities of half of the reflection sphere ($h,\pm k,\pm l$) were collected on an Enraf-Nonius CAD-4F diffractometer using an orange-yellow plate-shaped crystal, mounted on a glass fiber. The standard reflections were measured every hour of exposure time. There was no indication of decay during the data collection. The data were corrected for absorption and Lorentz–polarization effects and averaged in an unique data set following described procedure.[8] The resulting set contains two Friedel-related octants of reflections.

The structure was solved for the heavy atoms by combining information obtained from Patterson and direct methods (MULTAN 80),[9] completed by standard Fourier techniques, and refined by blocked full-matrix least-squares techniques using the SHELX-76 package.[10] Neutral atom scattering factors were taken from ref 11 and corrected for anomalous dispersion.[12] The structure including the non-hydrogen atoms was refined with

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Table II. Positional and Equivalent Isotropic Thermal Parameters for $[(\mu\text{-H})FeMn(CO)_6(t\text{-Bu-Pyca})]$

atom	x/a	y/b	z/c	$U(\text{eq})$,[a] Å^2
Fe	−0.12862 (3)	−0.39325 (1)	−0.69690 (1)	0.0335 (1)
Mn	−0.35266 (3)	−0.26545 (2)	−0.74490 (1)	0.0325 (1)
O(1)	−0.5099 (2)	−0.3980 (1)	−0.8671 (1)	0.0716 (5)
O(2)	−0.4641 (2)	−0.1074 (1)	−0.8564 (1)	0.0684 (5)
O(3)	−0.6472 (2)	−0.2693 (1)	−0.6450 (1)	0.0654 (5)
O(4)	−0.2724 (2)	−0.5601 (1)	−0.7835 (1)	0.0751 (6)
O(5)	−0.1569 (2)	−0.4385 (1)	−0.5104 (1)	0.0784 (6)
O(6)	0.1811 (2)	−0.4784 (1)	−0.7107 (1)	0.0740 (6)
N(1)	−0.2532 (2)	−0.1771 (1)	−0.6527 (1)	0.0342 (4)
N(2)	−0.1258 (2)	−0.2842 (1)	−0.7806 (1)	0.0312 (3)
C(1)	−0.4422 (2)	−0.3480 (1)	−0.8210 (1)	0.0474 (5)
C(2)	−0.4174 (2)	−0.1675 (1)	−0.8131 (1)	0.0440 (5)
C(3)	−0.5336 (2)	−0.2671 (1)	−0.6841 (1)	0.0438 (5)
C(4)	−0.2196 (2)	−0.4944 (1)	−0.7517 (1)	0.0475 (5)
C(5)	−0.1422 (2)	−0.4221 (1)	−0.5836 (1)	0.0476 (5)
C(6)	−0.0609 (2)	−0.4445 (1)	−0.7090 (1)	0.0462 (5)
C(7)	−0.0351 (2)	−0.2608 (1)	−0.7064 (1)	0.0338 (4)
C(8)	−0.0997 (2)	−0.1924 (1)	−0.6438 (1)	0.0335 (4)
C(9)	−0.0113 (2)	−0.1461 (1)	−0.5796 (1)	0.0437 (5)
C(10)	−0.0847 (3)	−0.0816 (1)	−0.5243 (1)	0.0516 (6)
C(11)	−0.2412 (3)	−0.0643 (1)	−0.5353 (1)	0.0534 (6)
C(12)	−0.3222 (2)	−0.1130 (1)	−0.5998 (1)	0.0439 (5)
C(13)	−0.0516 (2)	−0.2781 (1)	−0.8712 (1)	0.0399 (5)
C(14)	−0.0406 (3)	−0.1732 (1)	−0.8942 (1)	0.0635 (7)
C(15)	−0.1531 (3)	−0.3293 (2)	−0.9376 (1)	0.0647 (7)
C(16)	0.1112 (3)	−0.3217 (2)	−0.8752 (1)	0.0651 (7)
H(7)	0.071 (2)	−0.261 (1)	−0.708 (1)	0.040 (4)
H(9)	0.094 (2)	−0.164 (1)	−0.576 (1)	0.051 (5)
H(10)	−0.031 (3)	−0.052 (1)	−0.482 (1)	0.051 (6)
H(11)	−0.301 (3)	−0.018 (2)	−0.494 (1)	0.073 (7)
H(12)	−0.433 (3)	−0.107 (1)	−0.612 (1)	0.061 (6)
H(100)	−0.295 (2)	−0.351 (1)	−0.670 (1)	0.042 (5)
H(141)	−0.141 (3)	−0.140 (2)	−0.891 (1)	0.064 (6)
H(142)	0.011 (3)	−0.160 (2)	−0.945 (2)	0.076 (7)
H(143)	0.035 (3)	−0.141 (2)	−0.854 (2)	0.075 (7)
H(151)	−0.157 (3)	−0.393 (2)	−0.921 (2)	0.072 (7)
H(152)	−0.256 (3)	−0.306 (2)	−0.946 (2)	0.073 (7)
H(153)	−0.105 (3)	−0.321 (2)	−1.000 (1)	0.078 (7)
H(161)	0.150 (3)	−0.308 (2)	−0.940 (2)	0.070 (7)
H(162)	0.190 (3)	−0.285 (2)	−0.839 (2)	0.079 (7)
H(163)	0.100 (3)	−0.386 (2)	−0.858 (2)	0.096 (8)

[a] $U(\text{eq}) = {}^1/_3\Sigma_{ij}U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

isotropic temperature factors to $R = 0.068$. Refinement of the enantiomeric structure gave an R of 0.063, and further calculations were performed with it. Anisotropic refinement ended with $R = 0.035$. A subsequent ΔF synthesis located all hydrogen atoms; a peak (0.5 e Å^{-3}) at a distance of 1.72 Å from that of Mn and 1.66 Å from that of Fe was observed; in the vicinity of both metal atoms two satelite peaks (~0.5 e Å^{-3}) at a distance of 0.9 Å were visible. All hydrogens except the hydrido one were introduced into the refinement procedure with one overall temperature factor. The 002 reflection was excluded because of a bad $\Delta F/\sigma(F)$ value. An R of 0.025 was reached, and a ΔF synthesis revealed the hydrido atom at the same place as in the previous case. At this stage it was included into the refinement, and individual isotropic temperature factors were applied for all H atoms. A weighting function based on counting statistics and standard deviation in the reference reflection[13a] was introduced. Refinement of an isotropic extinction parameter did not improve the accuracy of the data. Therefore no extinction correction was applied. At this stage one more reflection (111; $\Delta F/\sigma(F) = 18$) was excluded from refinement. During all refinement procedures the differences in distances of hydrido to metal atoms remained in the range of the standard deviation given for the final values. A final ΔF synthesis did not show any features higher than 0.5 e Å^{-3}.

Listings of all bond angles, anisotropic thermal parameters, and observed and calculated structure factors and an ORTEP[13b] drawing of the molecule are included in the supplementary material.

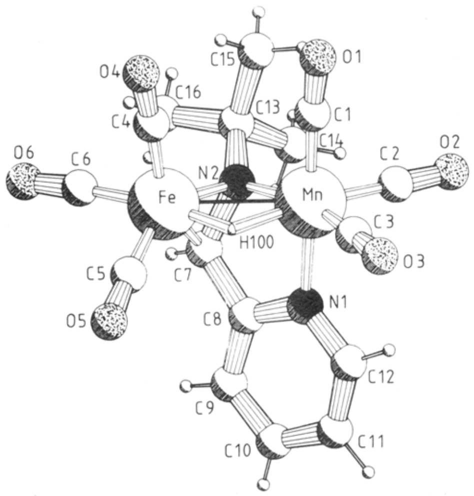

Figure 1. Molecular geometry of $[(\mu\text{-H})FeMn(CO)_6(t\text{-Bu-Pyca})]$ with the numbering of the atoms.

Analytical Data. All complexes gave satisfactory results (supplementary material). They showed characteristic ν(CO) IR absorptions, which are listed in Table IV. Mass spectra have been recorded by using a FD technique. Observed and calculated m/z values are also listed in Table IV (see also Figure 2).

Results

Molecular Structure. The crystal structure is composed of four discrete molecules in an orthorhombic non-

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Table III. Bond Lengths (Å) and Selected Bond Angles and Torsion Angles (deg) for [(μ-H)FeMn(CO)$_6$(t-Bu-Pyca)] with Esd's in Parentheses

Bond Lengths

Fe–Mn	2.7465 (3)	O(5)–C(5)	1.138 (2)	Mn–H(100)	1.73 (2)
Fe–C(4)	1.831 (1)	O(6)–C(6)	1.145 (2)	C(7)–H(7)	0.92 (2)
Fe–C(5)	1.765 (1)	N(1)–C(12)	1.348 (2)	C(9)–H(9)	0.95 (2)
Fe–C(6)	1.801 (2)	N(1)–C(8)	1.351 (2)	C(10)–H(10)	0.89 (2)
Fe–C(7)	2.045 (1)	N(2)–C(13)	1.515 (2)	C(11)–H(11)	1.05 (2)
Fe–N(2)	1.995 (1)	N(2)–C(7)	1.408 (2)	C(12)–H(12)	0.98 (2)
Mn–C(3)	1.814 (2)	C(7)–C(8)	1.464 (2)	C(14)–H(141)	0.99 (2)
Mn–N(2)	2.051 (2)	C(8)–C(9)	1.398 (2)	C(14)–H(142)	0.91 (3)
Mn–N(1)	2.060 (1)	C(9)–C(10)	1.391 (2)	C(14)–H(143)	1.01 (3)
Mn–C(1)	1.813 (1)	C(10)–C(11)	1.385 (4)	C(15)–H(151)	0.94 (2)
Mn–C(2)	1.815 (1)	C(11)–C(12)	1.384 (2)	C(15)–H(152)	0.96 (3)
O(1)–C(1)	1.153 (2)	C(13)–C(14)	1.527 (2)	C(15)–H(153)	1.03 (2)
O(2)–C(2)	1.146 (2)	C(13)–C(15)	1.517 (3)	C(16)–H(161)	1.05 (2)
O(3)–C(3)	1.147 (2)	C(13)–C(16)	1.538 (3)	C(16)–H(162)	1.02 (3)
O(4)–C(4)	1.141 (2)	Fe–H(100)	1.61 (2)	C(16)–H(163)	0.95 (2)

Bond Angles

Metal–Carbonyl Part

Mn–C(1)–O(1)	174.8 (2)	Mn–C(3)–O(3)	179.0 (1)	Fe–C(5)–O(5)	177.0 (2)
Mn–C(2)–O(2)	177.2 (2)	Fe–C(4)–O(4)	176.9 (1)	Fe–C(6)–O(6)	175.4 (1)

Around Mn

N(2)–Mn–C(1)	99.08 (7)	N(1)–Mn–C(1)	176.73 (6)	N(1)–Mn–N(2)	81.81 (6)
Fe–Mn–C(3)	117.74 (5)	C(1)–Mn–C(3)	86.87 (7)	C(3)–Mn–H(100)	84.7 (6)
Fe–Mn–N(2)	46.40 (4)	N(1)–Mn–C(3)	91.41 (7)	C(2)–Mn–H(100)	173.6 (6)
Fe–Mn–N(1)	85.76 (4)	N(1)–Mn–C(2)	92.87 (6)	C(1)–Mn–H(100)	95.3 (7)
Fe–Mn–C(2)	150.41 (5)	Fe–Mn–C(1)	92.57 (5)	N(1)–Mn–H(100)	81.8 (7)
N(2)–Mn–C(2)	104.11 (7)	C(1)–Mn–C(2)	89.96 (7)	N(2)–Mn–H(100)	78.8 (7)
C(2)–Mn–C(3)	91.83 (7)	N(2)–Mn–C(3)	162.91 (7)	Fe–Mn–H(100)	33.3 (7)

Ligand Part

C(8)–N(1)–C(12)	118.9 (1)	N(2)–C(7)–C(8)	117.3 (1)	C(10)–C(11)–C(12)	119.4 (2)
Mn–N(1)–C(12)	128.7 (1)	Fe–C(7)–N(2)	67.71 (8)	N(1)–C(12)–C(11)	121.9 (2)
Mn–N(1)–C(8)	112.3 (1)	Fe–C(7)–C(8)	114.2 (1)	C(14)–C(13)–C(15)	110.4 (1)
C(7)–N(2)–C(13)	118.1 (1)	N(1)–C(8)–C(9)	122.1 (1)	N(2)–C(13)–C(16)	113.6 (1)
Mn–N(2)–C(7)	107.0 (1)	C(7)–C(8)–C(9)	123.4 (1)	C(15)–C(13)–C(16)	108.2 (2)
Fe–N(2)–C(7)	71.52 (9)	N(1)–C(8)–C(7)	114.6 (1)	N(2)–C(13)–C(14)	106.7 (1)
Mn–N(2)–C(13)	129.4 (1)	C(8)–C(9)–C(10)	118.4 (2)	C(14)–C(13)–C(16)	108.9 (2)
Fe–N(2)–Mn	85.49 (6)	C(9)–C(10)–C(11)	119.3 (2)	N(2)–C(13)–C(15)	109.1 (1)
Fe–N(2)–C(13)	128.5 (1)				

Hydride Angle

Fe–H(100)–Mn	110 (1)

Around Fe

N(2)–Fe–C(7)	40.77 (6)	Mn–Fe–C(7)	69.96 (5)	Mn–Fe–N(2)	48.11 (5)
C(4)–Fe–C(5)	103.30 (7)	C(6)–Fe–C(7)	90.12 (7)	C(6)–Fe–H(100)	170.9 (7)
C(4)–Fe–C(6)	91.73 (7)	Mn–Fe–C(6)	151.58 (5)	C(4)–Fe–H(100)	91.4 (7)
C(4)–Fe–C(7)	148.62 (6)	N(2)–Fe–C(5)	142.67 (6)	N(2)–Fe–H(100)	83.4 (7)
Mn–Fe–C(4)	95.27 (5)	N(2)–Fe–C(6)	103.63 (7)	C(5)–Fe–H(100)	77.2 (7)
C(5)–Fe–C(6)	93.79 (7)	N(2)–Fe–C(4)	108.80 (6)	C(7)–Fe–H(100)	91.7 (7)
C(5)–Fe–C(7)	107.83 (6)	Mn–Fe–C(5)	111.21 (5)	Mn–Fe–H(100)	36.3 (7)

Torsion Angles

C(13)–N(2)–C(7)–C(8)	128.9 (1)	Mn–N(2)–C(7)–C(8)	−27.5 (2)
N(2)–C(7)–C(8)–N(1)	15.5 (2)	N(2)–Mn–N(1)–C(8)	−16.2 (1)
C(7)–C(8)–N(1)–Mn	5.5 (2)	N(1)–Mn–N(2)–C(7)	22.8 (1)

centrosymmetric unit cell. Figure 1 is a PLUTO drawing[14] of [(μ-H)FeMn(CO)$_6$(t-Bu-Pyca)] showing the molecular geometry and adopted atomic numbering. Bond lengths and selected bond and torsion angles are given in Table III.

A remarkable feature of the structure is the presence of a bridging hydride atom (H(100)). The μ-H bridge is of the closed MHM type,[15] with an asymmetrical, bent FeH(100)Mn bond. The Fe–H(100) bond length of 1.61 (2) Å is rather short for an Fe-bridging H bond but the Mn–H(100) distance (1.73 (2) Å) and the Fe–H(100)–Mn angle (110(1)°) are within the expected range.[16] Both metal atoms are approximately octahedrally surrounded with H(100) and imine N(2) bridging the metal–metal bond. The distortion of the octahedra can be seen from bond angles deviating from 180° or 90°. Deviation from linearity between two apical ligands is more pronounced in the Fe coordination array (C(7)–Fe–C(4) = 148.61 (1)° vs. N(1)–Mn–C(1) = 176.7 (1)°). The arrangement of equatorial ligands, especially of H(100) and N(2), contributes to the nonplanarity of the equatorial plane (C(5)–Fe–H(100) = 77.2 (7)°; C(6)–Fe–N(2) = 103.6 (1)°; C(3)–Mn–H(100) = 84.7 (7)°; C(2)–Mn–N(2) = 104.1 (1)°). The Fe–Mn bond length of 2.7465 (3) Å is normal for a single Fe–Mn bond.[17]

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[14] Spek, A. L. "The EUCLID Package" in "Computational Crystallography"; Sayre, D., Ed.; Clarendom Press: Oxford, 1982.

[15] Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

[16] Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

In other dinuclear FeMn complexes it varies between 2.84 Å in a nonbridged species[18] and 2.5393 (9) Å in a triply-bridged species.[19]

The metal carbonyl part consists of six terminal CO group bond angles ranging from 174.8 (2) to 179.0 (1)° and with three carbonyls bonded to each metal in an eclipsed conformation. Apart from the Fe–C(5) distance (1.765 (2) Å), which is fairly short, there is no significant difference in M–C(O) bond lengths between apically and equatorially positioned carbonyls (M–C(O) ranges from 1.801 (2) to 1.831 (2) Å). Both C(3) and C(5) carbonyl groups are cis to the hydrido ligand, but only the C(5) carbonyl reveals a shortening of the M–C bond distance.

The α-diimine ligand is coordinated to Mn via the pyridyl N(1) atom, occupying an apical site, and the imine N(2) atom, occupying an equatorial site, with about equal bond lengths of 2.060 (2) and 2.051 (2) Å, respectively. The C(7)=N(2) part is η^2-coordinated to Fe, with C(7) in an apical site and N(2) in an equatorial site and with only slightly different bond lengths of 2.045 (1) and 1.995 (1) Å, respectively. Taking the longer covalent radius of Ru with respect to Fe and Mn into consideration, these ligand–metal bond distances are analogous to those found in $[Ru_2(CO)_4(i\text{-Pr-Pyca})_2]$, containing also a six-electron-bonded Pyca ligand.[20] The chelating part of the ligand, together with Mn, closes a five-membered ring that exhibits a slightly twisted conformation. The pyridyl residue of the ligand is almost coplanar with the five-membered ring with a dihedral angle between the two least-squares planes of 7.2 (1)°.

The imine N(2)–C(7) bond length of the η^2-coordinated part of the α-diimine ligand is 1.408 (2) Å. For a normal $N(sp^2)=C(sp^2)$ double bond a bond length of about 1.27 Å is expected, and this is indeed found for the two imine bonds in free c-Hex-DAB, both being 1.258 (3) Å.[21] It has been observed that upon η^2-C=N coordination this bond distance is extensively lengthened to about 1.40 Å.[1b-f,22] Obviously, such a bond lengthening also occurs in the *t*-Bu-Pyca ligand in the present compound. However, both the small deviation from planarity of the α-diimine ligand system (torsion angle between the two imine bonds being 15.5 (2)°) and the bond angles around N(2) and C(7) (Table III; N(2)–C(7)–H(7) = 122 (1)°; C(8)–C(7)–H(7) = 114 (1)°) point to a sp^2 hybridization for these two imine atoms. This is analogous to the description of the η^2-C=N bonding situation in the isoelectronic complex $[CoMn(CO)_6(t\text{-Bu-DAB})]$, containing the six-electron-bonded α-diimine ligand *t*-Bu-DAB.[1c]

Table IV. IR and FD Mass Data

	M^a	$\nu(CO)^b$
$[(\mu\text{-H})FeM(CO)_6(R\text{-DAB}\{R_1,R_2\})]$		
M = Mn; R_1 = R_2 = H; R = *p*-tol	516 (516.2)	2061(m), 2017(s), 1995(s), 1914(s), 1933(m)^c
M = Re; R_1 = R_2 = H; R = *i*-Pr	552 (551.3)	2061(m), 2013(s), 1995(s), 1988(s), 1920(vs)
M = Re; R_1 = R_2 = H; R = c-Hex	632 (631.5)	2061(m), 2013(s), 1996(s), 1989(s), 1920(vs)
M = Re; R_1 = H, R_2 = CH_3; R = *i*=Pr	566 (565.4)	2061(m), 2014(s), 1994(s), 1986(s), 1919(vs)
$[(\mu\text{-H})FeM(CO)_6(R\text{-Pyca})]$		
M = Mn; R = *t*-Bu	442 (442.1)	2055(s), 2012(vs), 1987(s), 1979(s), 1929(vs)
M = Mn; R = *i*-Pr	428 (428.1)	2060 (s), 2015 (vs), 1995(s), 1987(s), 1923(vs)
M = Re; R = *i*-Pr	560 (559.3)	2060 (s), 2015 (vs), 1995(s), 1987(s), 1923(vs)

^{a} The observed *M* values account for the highest peak of the isotope pattern (^{187}Re 62.9 and ^{185}Re 37.1%; ^{56}Fe 91.7, ^{54}Fe 5.8, and ^{57}Fe 2.2%). The calculated values are given in parentheses. ^{b} cm^{-1} in hexane (vs, very strong; s, strong; m, medium; sh, shoulder). ^{c} In dichloromethane.

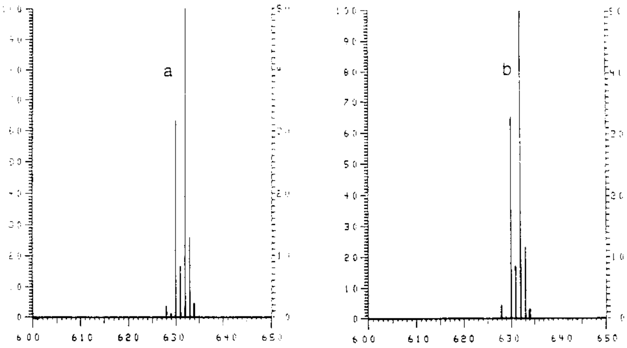

Figure 2. FD mass spectrum of $[(\mu\text{-H})FeRe(CO)_6(\text{c-Hex-DAB})]$: a, calculated; b, measured.

The central C(7)–C(8) distance of 1.464 (2) Å is normal for a single $C(sp^2)–C(sp^2)$ bond. In the free α-diimine ligand c-Hex-DAB a central C–C bond length of 1.457 (3) Å was found, based upon which it was concluded that no conjugation between the two imine bonds was present.[21] In the only other structure containing a six-electron bonded Pyca ligand, i.e., $[Ru_2(CO)_4(i\text{-Pr-Pyca})_2]$,[20] a C–C bond length of 1.454 (7) Å is found.

When one compares η^2-C=N coordination of R-DAB with that of R-Pyca, it is apparent that π-back-donation in the case of R-DAB lengthens the C=N double bond but also shortens the C—C central bond to about 1.40 Å. For R-Pyca one observes about the same lengthening for the imine C=N bond but hardly any effect with respect to the C—C bond (vide supra). This indicates that for R-Pyca the ligand orbital, which receives the electron density through π-back-donation, is much more than for R-DAB localized between one imine C and N atom only.

The coordination mode of the *t*-Bu-Pyca ligand in the present compound can best be described as being in between a six-electron σ-N, σ-N′, η^2-C=N′ and a six-electron σ-N, μ-N′, η^2-C=N′ bonding one. The difference in charge on both metals is counterbalanced by the presence of the asymmetric bridging H(100) ligand. In the isoelectronic

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(17) Some reported Fe–Mn single bond distances are as follows: (a) 2.616 (5) and 2.640 (4) Å in $[FeMn(CO)_6\{(t\text{-Bu})\overline{NC(H)C}(H)N(H)(t\text{-Bu})\}]$.[1a] (b) 2.748 (1) and 2.706 (1) Å in $[(C_5H_5)(CO)_2MnFe_2(CO)_6(\mu_3\text{-}PC_6H_{11})]$: Schneider, J.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1982**, *115*, 989. (c) 2.618 (1) Å in $(\mu\text{-}CH_2)(\mu\text{-}CO)[(C_5H_5)(CO)FeMN(CO)_4]$: Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607. (d) 2.760 (4) Å in $[(C_5H_5)(CO)_2MnC(CO)CHPh]Fe(CO)_3$: Andrianov, V. G.; Struchkov, Y. T.; Kolobova, N. E.; Antonova, A. B.; Obezyuk, N. S. *J. Organomet. Chem.* **1976**, *122*, C33. (e) 2.561 (1) and 2.577 (1) Å in $[(C_5H_5)(CO)_2(C(H)C(COOMe))MnFe_2(CO)_6]$: Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *231*, 37. (f) 2.703 (4) Å in $[(C_5H_5)(CO)_2Mn[\mu_2\text{-}C{=}CHOOMe)Fe(CO)_4]$: Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Aleksandrov, G. G.; Struchkov, Y. T. *Ibid.* **1982**, *228*, 265.

(18) In $[(C_5H_5)(CO)_2FeMn(CO)_5]$ a bond length of 2.84 Å is found: Hansen, P. J.; Jacobsen, R. A. *J. Organomet. Chem.* **1966**, *6*, 389.

(19) In $[(\mu\text{-H})FeMn(CO)_6\{\mu,\mu'\text{-N}(p\text{-tol})CH_2CH_2N(p\text{-tol})\}]$ a very short bond length of 2.5393 (9) Å is found.[1g]

(20) Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H., to be submitted for publication.

(21) Keijsper, J.; van der Poel, H.; Polm, L. H.; van Koten, G.; Vrieze, K.; Seignette, P. F. A. B.; Varenhorst, R.; Stam, C. H. *Polyhedron* **1983**, *2*, 1111.

(22) Fruehauf, H. W.; Landers, A.; Goddard, R.; Krueger, C. *Angew. Chem.* **1978**, *90*, 56.

Table V. ^{1}H NMR Data (δ)[a]

	R group[b]	μ-H	imine H
[(μ-H)FeM(CO)$_6$(R-DAB{R$_1$,R$_2$})]			
M = Mn; R$_1$ = R$_2$ = H; R = *p*-tol[f]	2.36 (s, 3 H), 2.42 (s, 3 H), 7.5–6.9 (m, 8 H)	−17.77 (s, 1 H)	3.80 (d,[c] 1 H), 7.97 (d,[c] 1 H)
M = Re; R$_1$ = R$_2$ = H; R = *i*-Pr	3.49 (sept,[d] 1 H), 2.82 (sept,[d] 1 H), 1.56 (d,[d] 3 H), 1.43 (d,[d] 3 H), 1.21 (d,[d] 3 H)/1.09 (d,[d] 3 H)	−16.48 (s, 1 H)	4.01 (d,[c] 1 H), 8.03 (d,[c] 1 H)
M = Re; R$_1$ = R$_2$ = H; R = c-Hex[f]	2.89 (m, 1 H), 2.40 (m, 1 H), 2–1 (br, 20 H)	−16.03 (s, 1 H)	3.62 (d,[c] 1 H), 7.20 (d,[c] 1 H)
M = Re; R$_1$ = H; R$_2$ = CH$_3$; R = *i*-Pr	0.97 (d,[d] 3 H)/1.26 (d,[d] 3 H), 1.43 (d,[d] 3 H)/1.53 (d,[d] 3 H), 2.75 (sept,[d] 1 H), 3.55 (sept,[d] 1 H), 1.99 (s, 3 H)	−16.40 (s, 1 H)	4.11 (s, 1 H)

	R group	Pyca	μ-H	imine H
[(μ-H)FeM(CO)$_6$(R-Pyca)]				
M = Mn, R = *t*-Bu[f]	1.54 (s, 9 H)	6.03 (vt,[d] 1 H), 6.40 (d,[e] 1 H), 6.71 (vt,[e] 1 H), 7.91 (d,[d] 1 H)	−17.27 (s, 1 H)	3.81 (s, 1 H)
M = Mn, R = *i*-Pr[f]	2.67 (sept,[d] 1 H), 1.34 (d,[d] 3 H)/1.58 (d,[d] 3 H)	5.96 (vt,[d] 1 H), 6.61 (d,[e] 1 H), 6.78 (vt,[e] 1 H), 7.96 (d,[d] 1 H)	−15.66 (s, 1 H)	4.29 (s, 1 H)
M = Re, R = *i*-Pr	2.86 (sept,[d] 1 H), 1.42 (d,[d] 3 H)/1.49 (d,[d] 3 H)	6.79 (vt,[d] 1 H), 7.32 (d,[e] 1 H), 7.54 (vt,[e] 1 H), 8.31 (d,[d] 1 H)	−16.10 (s, 1 H)	4.63 (s, 1 H)

[a] The values in ppm (multiplicity, integral) have been obtained in CDCl$_3$ solution. [b] Vertical bars separate diastereotopic pairs; s = singlet, d = doublet, sept = septet, m = multiplet, vt = virtual triplet. [c] J = 2 Hz. [d] J = 6 Hz. [e] J = 8 Hz. [f] In toluene-d_8.

species [CoMn(CO)$_6$(*t*-Bu-DAB)] an analogous situation was found:[1c] the bonding mode of the α-diimine ligand being in between the two extreme six-electron ones, the charge distribution being ruled by the presence of a semibridging carbonyl.

IR ν(CO) Region. All [(μ-H)FeM(CO)$_6$(α-diimine)] complexes show characteristic absorption patterns in the (CO) region (see Table IV). They exhibit five, one of which is broad, to six bands between 2065 and 1920 cm^{-1}, due to six terminal CO groups. All complexes give comparable spectra, indicating similar metal carbonyl parts.

FD Mass Spectroscopy. The heterodinuclear character of the [(μ-H)FeM(CO)$_6$(α-diimine)] complexes is clearly indicated by the isotope pattern found in their FD mass spectra (see Figure 2). As is usual, the molecular ion is observed to have the highest intensity. Only for M = Re and α-diimine = *i*-Pr-DAB{H,CH$_3$} are small peaks due to the [M − CO]$^{+\cdot}$ ion also observed. The results are summarized in Table IV and are in accord with the calculated molecular weights.

^{1}H NMR Spectroscopy. The ^{1}H NMR data are listed in Table V.

The α-Diimine Ligand. In free R-DAB or R-Pyca the imine protons absorb at about 8 ppm, and this resonance position is hardly changed when only σ-N coordination is present.[1a–f] For R-DAB use of the π electrons for coordination results in a dramatic upfield shift. Thus six-electron coordination of R-DAB results in asymmetry in the ligand, and accordingly an AX pattern for the protons is observed. The proton at the η^2-C(H)=N bonded part then absorbs at ±4 ppm.

In the present [(μ-H)FeM(CO)$_6$(R-DAB)] compounds the observation of both an AX pattern for the imine protons and of an inequivalency for the two R groupings is in line with an asymmetric six-electron bonding mode for the R-DAB ligand. The one singlet at about 4 ppm for the imine proton of [(μ-H)FeM(CO)$_6$(R-Pyca)] clearly indicates that the C(H)=N part of the R-Pyca ligand is η^2-coordinated just as found in the solid-state structure of [(μ-H)FeMn(CO)$_6$(*t*-Bu-Pyca)]. The pyridylic protons absorb at their expected resonance positions.[20] For isoelectronic M$_2$(CO)$_6$(R-DAB)[1d,22] and M$_2$(CO)$_6$(R-Pyca)[20] (M = Fe, Ru) complexes similar resonance values for the α-diimine ligands were found as those obtained for the present compounds.

When [Re(CO)$_3$(*i*-Pr-DAB{H,CH$_3$})Br] is reacted with [HFe(CO)$_4$]$^-$, formation of two isomeric products can be expected. ^{1}H NMR spectroscopy indicates that only the one with the C(H)=N imine double bond being η^2-coordinated is isolated; no evidence for the formation of the other isomer, with an η^2-C(CH$_3$)=N coordinated double bond, is found. This observation is in line with our earlier conclusion that η^2-coordination of a C(H)=N bond is thermodynamically more favorable than that of a C(CH$_3$)=N bond.[1c]

The Bridging Hydride. Generally, the chemical shift of a bridging hydride is at slightly higher field than that of a terminal one.[23] The observation of one singlet at about −16 ppm (see Table V) for the present compounds is in accord with a hydride bridging the two metals, just as found in the solid-state structure.

^{13}C NMR Spectroscopy. The ^{13}C NMR data are listed in Table VI.

The α-Diimine Ligand. The trend for the chemical shift of the imine C atoms is the same as that for the chemical shifts of the imine H atoms discussed above. Thus in free R-DAB or R-Pyca the imine C atoms absorb at about 170 ppm. σ-N coordination does not alter this position very much but η^2-C=N coordination causes an extreme upfield shift. Accordingly, in six-electron-coordinated R-DAB complexes the C atom of the η^2-C=N bonded part of the ligand absorbs between 60 and 90 ppm.[24]

In the spectra of the present R-DAB complexes the imine C atoms are found at about 70 and 180 ppm, while the two R groupings are also magnetically inequivalent. Both observations are in line with an asymmetric six-electron coordination mode of the ligand. The imine carbon atom of the R-Pyca derivatives also resonate at about 70 ppm, being in line with a η^2-C=N bonded imine group. In isoelectronic [M$_2$(CO)$_6$(R-Pyca)] (M = Fe, Ru), the chemical shifts of the imine carbons are comparable:[20]

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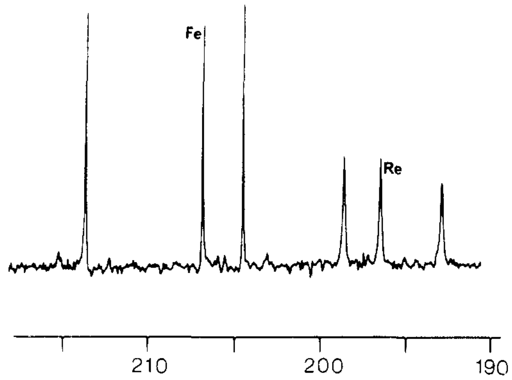

Figure 3. Carbonyl region of the ^{13}C NMR spectrum of [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB{H,CH$_3$})].

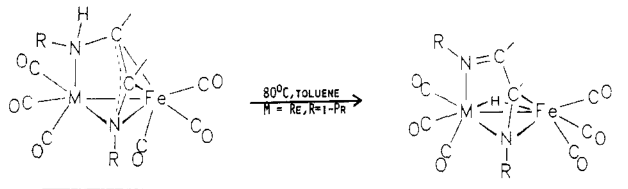

Figure 4. proton migration from the ligand to the metal carbonyl core in the formation reaction of [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB)].

64.2 ppm (M = Fe, R = *t*-Bu), 61.2 ppm (M = Ru, R = *t*-Bu). The pyridyl carbon atoms C_2–C_6 are found at their expected values (see Table VI, which also shows the numbering of the C atoms).

The ^{13}C NMR spectrum of the reaction product of [Re(CO)$_3$(*i*-Pr-DAB{H,CH$_3$})Br] with [HFe(CO)$_4$]$^-$ indicates just as the ^{1}H NMR spectrum did (vide supra) that only one of the two possible isomers is formed. Again, only one pattern of a six-electron bonded DAB ligand is observed.

The Carbonyls. Only for a few compounds could the carbonyl resonances be detected. The asymmetry in coordination of the α-diimine ligand results in an inequivalence of the six carbonyls. Thus in a rigid metal carbonyl skeleton this should lead to six different resonance positions. Indeed six peaks are observed in the carbonyl region indicating that only slow, if any, carbonyl scrambling occurs in the present compounds. The spectra do not change in the temperature range −40 to +35 °C. In Figure 3 the carbonyl part of the spectrum of [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB{H,CH$_3$})] is shown.

The three singlets at 192.1, 195.8, and 198.1 ppm are assigned to the three carbonyls on Re and the remaining three lower field absorptions, grouped around 208 ppm, to those on Fe. This assignment is in accord with literature findings[25] and with the observation that for dinuclear FeMn complexes the carbonyls on Fe resonate at about 205–215 ppm and the Mn carbonyls at 215–220 ppm;[1a,g] in these complexes no resonances are found below 200 ppm.

The Formation of [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB)]. Isolated [FeRe(CO)$_6$$\{(i\text{-Pr})\overline{\mathrm{NC(H)C}}\mathrm{(H)N(H)}(i\text{-Pr})\}$] reacts, when heated in toluene, to yield the isomeric hydride [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB)] (see Figure 4).

The reaction at 80 °C was followed with ^{1}H NMR and FT-IR spectroscopy. The rate constant *k* of the reaction was calculated by measuring the integrals of the ^{1}H NMR peaks due to the starting complex at ambient time intervals. The reaction was found to be first order (five measurements, correlation coefficient for the least-squares line: $\epsilon = 0.997$) with $k = 8.5 \times 10^{-5}$ l^{-1} s^{-1}. According to the Eyringh equation this corresponds to a standard free energy of activation $\Delta G^* = 27$ kcal/mol. In Figure 5 the first ($t = 0$, starting complex) and subsequent ^{1}H NMR spectra are shown.

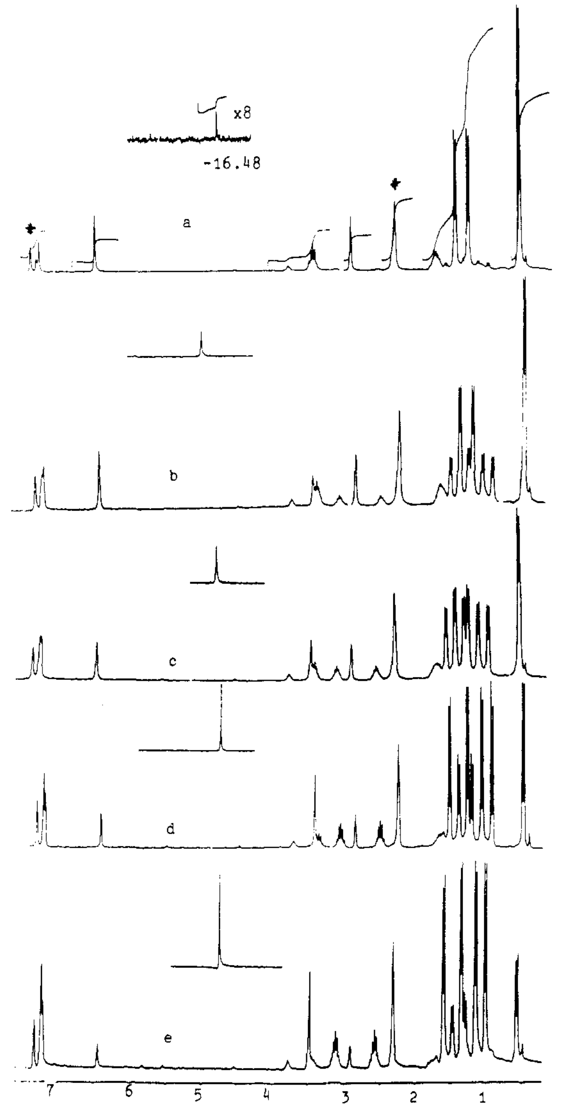

Figure 5. Isomeric rearrangement reaction followed with ^{1}H NMR spectroscopy: a, 0 h; b, 0.75 h; c, 1.5 h; d, 2.8 h; e, 5 h (the asterisks indicate peaks due to toluene).

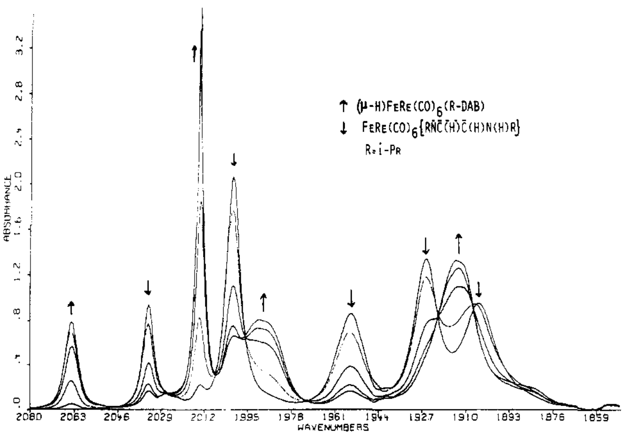

Figure 6. Isomeric rearrangement reaction followed with FT-IR spectroscopy: ↑, peaks belonging to [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB)]; ↓, peaks belonging to [FeRe(CO)$_6$$\{(i\text{-Pr})\overline{\mathrm{NC(H)C}}\mathrm{(H)N(H)}(i\text{-Pr})\}$].

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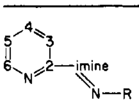
Table VI. ^{13}C NMR Data (δ)[a]

compd	imine C	C_2	C_3	C_4	C_5	C_6	R group[b]	CO
								
R = *t*-Bu	155.6	154.9	136.7	123.6	120.2	148.4	57.0, 28.9	
[(μ-H)FeM$(CO)_6$(R-Pyca)]								
M = Mn; R = *t*-Bu	62.3	171.2	136.7	119.1	117.3	151.5	64.0, 32.9	
M = Mn; R = *i*-Pr	68.6	170.5	136.7	119.0	117.5	151.7	68.7, 28.3/25.9	
M = Re; R = *i*-Pr	70.3	170.9	137.8	120.3	118.5	152.3	67.8, 28.0/26.5	191.8, 195.6, 197.5, 204.0, 206.9, 212.5

	imine C	*i*-Pr group[b]	CH_3	CO
[(μ-H)FeRe$(CO)_6$(*i*-Pr-DAB{CH_3,H})]	184.8, 74.7	67.5, 54.1, 28.0/26.8, 24.7/19.9	15.8	192.1, 195.8, 198.1, 204.3, 206.7, 213.8

[a] The values (ppm, relative to Me_4Si) have been obtained in $CDCl_3$ solution at 35 °C. [b] Vertical bars separate diastereotopic pairs.

When the reaction is followed with FT-IR spectroscopy (ν(CO) region), one observes a smooth disappearance of the peaks due to the starting complex and concomitantly a growing of the product's peak. The occurrence of various isobestic points indicates that the reaction is very clean (see Figure 6).

Discussion

Reaction Mechanism. $[HFe(CO)_4]^-$ reacts with [M$(CO)_3$(α-diimine)Br] to yield the heterodinuclear hydride species, according to eq 1.

$$[M(CO)_3(\alpha\text{-diimine})Br] \xrightarrow[-CO,-Br]{[HFe(CO)_4]^-} [(\mu\text{-H})FeM(CO)_6(\alpha\text{-diimine})] \quad (1)$$

Generally, when [M$(CO)_3$(α-diimine)Br] is reacted with $[HFe(CO)_4]$, two different types of products are obtained, depending on both M and the type of α-diimine. (i) For M = Mn and Re and α-diimine = R-Pyca, exclusively [(μ-H)FeM$(CO)_6$(R-Pyca)] is obtained while for M = Re and α-diimine = R-DAB, the analogous compound [(μ-H)FeRe$(CO)_6$(R-DAB)] is primarily formed (this study). (ii) For M = Mn and α-diimine = R-DAB, the 3-(R-amino)-1-R-azaallylic derivative [FeMn$(CO)_6${RNC(H)C(H)N(H)R}] is primarily obtained.[26]

In general, for a reaction of a carbonyl metalate with a metal halide, several reaction routes have to be considered.[27] The reaction between $[HFe(CO)_4]^-$ and [M$(CO)_3$(α-diimine)Br] is very clean and only heterodinuclear products in relatively high yield are obtained. Therefore, a substitution reaction, replacing Br^- by $[HFe(CO)_4]^-$, is strongly indicated to be the first step in the reaction sequence. During this step the hetero metal–metal bond is formed while the α-diimine ligand remains coordinated to M only. No direct evidence, however, was found for the supposed [$(CO)_4$(H)FeM$(CO)_3$(α-diimine)] intermediate. After this first substitution step, two different reaction routes are possible: The first route is a carbonyl elimination from Fe, thereby creating an empty site which is filled by η^2-coordination of one C═N bond of the α-diimine ligand. A small rearrangement, in which the hydride becomes asymmetrically bridging, then yields the final hydride product. Such a reaction route is strongly indicated for α-diimine = R-Pyca but may also be present, besides the mechanism discussed below, for the R-DAB derivatives.

Second and probably competing with the first discussed reaction route, a C═N insertion into the Fe–H bond may take place, to be followed by CO elimination from Fe and concomitant η^2-coordination of the second C═N bond to Fe.[28] During this reaction the neutral α-diimine ligand is converted into a monoanionic 3-amino-1-azaallyl ligand which is σ-N,σ-N′ bonded to M and η^3-bonded to Fe. For α-diimine = R-Pyca, such a subsequent conversion is not possible because one imine bond is resonance stabilized. The resulting 3-amino-1-azaallylic products are stable for M = Mn and α-diimine = R-DAB, and several derivatives have been isolated.[1a] For M = Re the reaction continues and a subsequent step may yield the hydride [(μ-H)FeRe$(CO)_6$(R-DAB)] products. This step, which is only proved to be present for R = *i*-Pr (vide supra), may be a deinsertion reaction, bringing the H atom from the N atom back to the bimetallic carbonyl unit (see Figure 4). Another possibility is that this proton migration occurs via an intermediate type of 2e–3c interaction between the amine N, the amine H, and the Fe atom in a way that is analogous to that found in [Mn$(CO)_3$$(C_6H_9)$].[29] This possibility, however seems to be less likely because, in the 3-amino-1-azaallylic products, Fe is already coordinatively saturated, whereas the Mn atom in [Mn$(CO)_3$$(C_6H_9)$] is not.

When [Mn$(CO)_3$(*i*-Pr-DAB{H,CH_3})Br] is reacted with $[HFe(CO)_4]^-$, a mixture of [FeMn$(CO)_6${(*i*-Pr)NC(H)C(CH_3)N(H)(*i*-Pr)}] and [FeMn$(CO)_6${(*i*-Pr)NC(CH_3)C(H)N(H)(*i*-Pr)}] is obtained. Reaction of [Re$(CO)_3$(*i*-Pr-DAB{H,CH_3})Br] with $[HFe(CO)_4]^-$ yields one isomer only, [(μ-H)FeRe$(CO)_6$(*i*-Pr-DAB{H,CH_3})], containing the C(H)═N part η^2 bonded to Fe. If the latter reaction proceeds via the first discussed reaction route, then, after CO elimination from Fe, indeed only the C(H)═N imine bond will become η^2 bonded to Fe.[1c] When, however, the reaction proceeds via the second discussed route, i.e., via the 3-amino-1-azaallylic intermediate, according to the results of the reaction of $[HFe(CO)_4]^-$ with [Mn$(CO)_3$(*i*-Pr-DAB{H,CH_3})Br] (vide supra), both isomeric 3-amino-1-azaallylic intermediates and thus also both [(μ-H)FeRe$(CO)_6$-

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(26) A third type of product (see Introduction) is obtained from the reaction of [Mn$(CO)_3$(*p*-tol-DAB)Br] with excess $[HFe(CO)_4]^-$. Full details about the resulting [(μ-H)FeMn$(CO)_6${μ,μ'-N(*p*-tol)CH_2CH_2N(*p*-tol)}] compound, including its molecular geometry, will be published soon.[1g]

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(28) Other possible reaction mechanisms, leading to the 3-amino-1-azaallylic products, are discussed elsewhere.[1a]

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Organometallics 1985, *4*, 446-457

(*i*-Pr-DAB{H,CH$_3$})] isomers will be formed. The final rearrangement, in which the η^2-coordination of the C(CH$_3$)=N moiety is replaced by that of the C(H)=N part, is then likely to be very rapid. The fact that only the one isomer with the C(H)=N part being η^2 bonded is obtained is in line with our earlier findings that an η^2-C(H)=N arrangement is thermodynamically more stable than an η^2-C(CH$_3$)=N one.[1c]

Conclusions

For the first time, mixed-metal carbonyl R-DAB hydride compounds have been isolated.

Neutral R-DAB may be partly reduced to anionic 3-amino-1-azaallyl and reformed again by oxidation; this is accompanied by a hydride migration from the metal carbonyl core to the R-DAB ligand and vice versa.

R-Pyca is able to use its C=N imine bond for η^2-coordination. Thus, just as R-DAB, R-Pyca can act as a six-electron donor in a σ-N,σ-N′, η^2-C=N′ bonding mode.

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Registry No. [(μ-H)FeMn(CO)$_6$(*p*-tol-DAB{H,H})], 94024-85-8; [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB{H,H})], 94024-86-9; [(μ-H)FeRe(CO)$_6$(*c*-Hex-DAB{H,H})], 94024-87-0; [(μ-H)FeRe(CO)$_6$(*i*-Pr-DAB{Me,Me})], 94024-88-1; [(μ-H)FeMn(CO)$_6$(*t*-Bu-Pyca)], 94024-89-2; [(μ-H)FeMn(CO)$_6$(*i*-Pr-Pyca)], 94024-90-5; [(μ-H)FeRe(CO)$_6$(*i*-Pr-Pyca)], 94024-91-6; [Mn(CO)$_3$(*p*-tol-DAB{H,H}Br], 70708-87-1; [Re(CO)$_3$(*i*-Pr-DAB{H,H})Br], 75548-79-7; [Re(CO)$_3$(*c*-Hex-DAB{H,H})Br], 75548-78-6; [Re(CO)$_3$(*i*-Pr-DAB{Me,Me})Br], 94024-92-7; [Mn(CO)$_3$(*t*-Bu-Pyca)Br], 94024-93-8; [Mn(CO)$_3$(*i*-Pr-Pyca)Br], 94024-94-9; [Re(CO)$_3$(*i*-Pr-Pyca)Br], 78214-58-1; [FeRe(CO)$_6${(*i*-Pr)NC(H)C(H)N(H)(*i*-Pr)}], 91443-27-5; Na[HFe(CO)$_4$], 53558-55-7.

Supplementary Material Available: Listings of observed and calculated structure factors, bond angles, and the final anisotropic thermal parameters, elemental analyses, and an ORTEP drawing of [(μ-H)FeMn(CO)$_6$(*t*-Bu-Pyca)] (27 pages). Ordering information is given on any current masthead page.

Metal Exchange Reactions under the Influence of a Cyclophosphazene Template: Iron, Cobalt, and Rhodium Metallophosphazenes[1]

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The use of a cyclophosphazene ring as a template for the construction of transition-metal dimers or clusters is described. The thermal reactions of a spiro diiron octacarbonyl bonded phosphazene (**2**) with Co$_2$(CO)$_8$, CoCp(CO)$_2$, or RhCp(CO)$_2$ (Cp = η^5-C$_5$H$_5$) lead to the formation of spiro-metallo or metallo cluster phosphazenes in which phosphorus–iron bonds have been replaced by phosphorus–cobalt or phosphorus–rhodium bonds. Reaction of **2** with Co$_2$(CO)$_8$ yields the mixed-metal cluster **4** in which two cobalt atoms are covalently bound to the bridging phosphazenyl phosphorus atom and the iron atom is coordinatively linked to the ring nitrogen atom. Reaction of **2** with CoCp(CO)$_2$ results in the formation of a phosphazene-bound Fe–Co dimer (**5**) and a phosphazene-bound Co–Co dimer (**6**). Similarly, **2** reacts with RhCp(CO)$_2$ to yield a phosphazene-bound Rh–Rh dimer (**7**). The reaction of **5** with RhCp(CO)$_2$ also leads to the formation of **7**, with no evidence for the formation of any Fe–Rh or Co–Rh dimeric species. The new metallophosphazene compounds were characterized by ^{31}P NMR, Mössbauer, infrared, and mass spectral techniques and by X-ray crystal structure analyses. These small molecule metallophosphazenes are model systems for the corresponding linear high polymers.

Although the field of metal cluster chemistry has been the focus of widespread research during the past 15 years,[2-14] several important questions remain to be answered. Two of these are the subject of this paper. First, how can the synthetic chemist construct mixed-metal clusters with reasonable certainty that specific metals will occupy predetermined sites? It is now well-known *how* hetero metals may be introduced into a cluster, but not known with any certainty *where* they will go. Second, how can the chemist use metal cluster chemistry in conjunction with high polymer chemistry to synthesize macromolecules that have exceptional catalytic or unusual electroactive properties? Possible answers to these questions have become available at the interface between transition metal

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(1) For an earlier paper on organometallic phosphazenes, see: Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337.

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