Table I. Electronic Spectral Data and Transition Assignments

Complex	ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
Mn$_2$(CO)$_{10}$[a]	26 700	2 900	d$\pi \rightarrow \sigma^*$
	29 740	33 700	$\sigma \rightarrow \sigma^*$
Mn$_2$(CO)$_8$(PPh$_3$)$_2$[a]	27 400	31 800	$\sigma \rightarrow \sigma^*$
Co$_2$(CO)$_8$[b]	23 470[c]	980	d$\pi \rightarrow \sigma^*$ (nonbridged)
	28 570[c]	5 500	$\sigma \rightarrow \sigma^*$ (nonbridged)
	35 460[c]	14 400	$\sigma \rightarrow \sigma^*$ (bridged)
	26 460[d]	2 200	d$\pi \rightarrow \sigma^*$ (bridged)
	(29 000)[d]	(3 700)	e
	(32 100)[d]	(13 500)	e
	35 460[d]	22 600	$\sigma \rightarrow \sigma^*$ (bridged)
Co$_2$(CO)$_6$(PPh$_3$)$_2$[f]	22 200(sh)	5 300	d$\pi \rightarrow \sigma^*$
	25 450	23 800	$\sigma \rightarrow \sigma^*$
Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$[g]	20 800[h]	h	d$\pi \rightarrow \sigma^*$
	27 780[g]	24 000[g]	$\sigma \rightarrow \sigma^*$

[a] In 3-pip at 77 K; from ref 6. [b] In 2-methylpentane; ϵ/Co$_2$ (total) values are reported. [c] 298 K. [d] 50 K; uncorrected for solvent contraction. [e] Not assigned. [f] In dichloromethane at 298 K. [g] In isooctane at 298 K. [h] Shoulder, observable only in low-temperature spectrum; cf. Figure 1.

Table II. Near-UV $\sigma \rightarrow \sigma^*$ Band Maxima for Several Metal–Metal Bonded Complexes

Complex	Calcd $\bar{\nu}$, cm^{-1} [a]	Obsd $\bar{\nu}$, cm^{-1} [a,b]
Mn$_2$(CO)$_{10}$		29 240 (342)[c]
Re$_2$(CO)$_{10}$		31 950 (313)[c]
(η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$		25 770 (388)[d]
(η^5-C$_5$H$_5$)$_2$W$_2$(CO)$_6$		27 620 (362)[d]
(η^5-C$_5$H$_5$)Mo(CO)$_3$Mn(CO)$_5$	27 505 (364)	26 810 (373)[e]
(η^5-C$_5$H$_5$)Mo(CO)$_3$Re(CO)$_5$	28 860 (347)	27 400 (365)[e]
(η^5-C$_5$H$_5$)W(CO)$_3$Mn(CO)$_5$	28 430 (352)	27 620 (362)[e]
(η^5-C$_5$H$_5$)W(CO)$_3$Re(CO)$_5$	29 785 (336)	30 210 (331)[e]
Co$_2$(CO)$_8$ [bridged]		35 460 (282)[f]
Co$_2$(CO)$_8$ [nonbridged]		28 570 (350)
Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$		27 780 (360)
Co$_2$(CO)$_6$(PPh$_3$)$_2$		25 450 (393)[g]
Co(CO)$_3$(PPh$_3$)Mn(CO)$_5$	27 345 (366)	26 600 (376)
(η^5-C$_5$H$_5$)Mo(CO)$_3$Co(CO)$_4$	27 170 (368)	28 170 (355)
(η^5-C$_5$H$_5$)W(CO)$_3$Co(CO)$_4$	28 095 (356)	29 240 (342)

[a] Wavelengths in nm are given in parentheses. [b] All measurements were made at 298 K in aliphatic hydrocarbon solvents unless noted otherwise. [c] From ref 11. [d] From ref 12. [e] From ref 14. [f] 50 K. [g] Dichloromethane at 298 K.

can infer that our ability to predict the M–M' $\sigma \rightarrow \sigma^*$ position from that of M–M and M'–M' implies little ionic bonding in the heterodinuclear complexes reported here.

Experimental Section

Complexes. Co$_2$(CO)$_8$ is commercially available and was used after sublimation. Both Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$ and Co$_2$(CO)$_6$(PPh$_3$)$_2$ were prepared according to published procedures[18] and infrared spectra in the carbonyl stretching region were found to be as reported previously.[18] The mixed-metal dinuclear complexes Mn(CO)$_5$Co-(CO)$_3$PPh$_3$ and (η^5-C$_5$H$_5$)M(CO)$_3$Co(CO)$_4$ (M = Mo, W) were prepared by near-UV irradiation of the homodinuclear metal–metal bonded complexes. A procedure analogous to that outlined for other M–M' complexes was used.[14] The compounds were purified by column chromatography and were characterized by infrared and UV–VIS spectra and by elemental analyses. The details are to be published in a paper concerning the photochemistry of M–Co bonded complexes.[19]

Spectra. Spectra of the complexes were recorded in optically transparent solvents using a Cary 17 UV–VIS–near-IR spectrophotometer. Low-temperature spectra were recorded in either 2-methylpentane, 2-methyltetrahydrofuran, or EPA (5:5:2 diethyl ether–isopentane–ethanol by volume). These solvents form good glasses at low temperature. The 77-K spectra were recorded using an all-quartz liquid N$_2$ Dewar fitted with optical-quality flats for windows. Lower temperature spectra were obtained using a Cryogenics Technology, Inc., cryotip assemply. All of the complexes studied here are light sensitive in solution. Special precautions were taken to exclude light. Solutions of Co$_2$(CO)$_8$ were cooled in a dry ice–acetone bath

to avoid thermal decomposition.

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Hydrogen–Deuterium Exchange in Transition Metal Hydridocarbonyl Cluster Complexes. Standardization of a Mass Spectroscopic Analytical Technique

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Although hydridometal cluster complexes are thermodynamically acidic,[1] a number of these such as H$_3$Re$_3$(CO)$_{12}$[2] or H$_4$Ru$_4$(CO)$_{12}$[3] ionize or exchange protons slowly in polar solvents and thus their reactions with bases are rather slow.

Table I. Mass Spectral Analysis of the Parent Ion of $HRe_3(CO)_{14}$[a]

Mass	I(calcd)[b]	I(obsd)[c,d]	I(calcd) $-I$(obsd)
948	4.21	3.58 (41)	0.63
949	0.68	0.78 (17)	−0.10
950	21.63	22.22 (189)	−0.61
951	3.50	3.07 (38)	0.43
952	37.30	41.64 (246)	−4.36
953	6.02	4.87 (61)	1.15
954	22.11	20.09 (169)	2.01
955	3.54	2.89 (34)	0.65
956	0.87	0.81 (15)	0.06
957	0.11	0.00 (0)	0.11
958	0.02	0.00 (0)	0.02

[a] R factor for average scan 10.1%; average R factor[d] 11.7 (38)%; average least-squares fit composition[c] 99.8 (6)% $HRe_3(CO)_{14}$ and 0.2 (6)% $Re_3(CO)_{14}$. [b] For composition of 100% $HRe_3(CO)_{14}$ and 0% $Re_3(CO)_{14}$. [c] Standard deviation ($\sigma = [(\Sigma x_i^2 - N\bar{x}^2)/(N - 1)]^{1/2}$) of least significant digits given in parentheses. [d] Average of 12 scans.

Table II. Mass Spectral Analysis of the Parent Ion of $DRe_3(CO)_{14}$[a]

Mass	I(calcd)[b]	I(obsd)[c,d]	I(calcd) $-$ I(obsd)
948	0.13	0.32 (14)	−0.19
949	4.11	3.96 (28)	0.15
950	1.31	2.00 (16)	−0.69
951	21.08	19.15 (137)	1.92
952	4.52	5.08 (35)	−0.56
953	36.36	40.66 (340)	−4.31
954	6.51	6.32 (18)	0.18
955	21.56	18.45 (112)	3.10
956	3.46	3.12 (22)	0.34
957	0.85	0.90 (15)	−0.05
958	0.11	0.00 (0)	0.11
959	0.02	0.00 (0)	0.02

[a] R factor for average scan 11.6%; average R factor[d] 12.5 (62)%; average least-squares fit composition[c] 96.5 (30)% $DRe_3(CO)_{14}$, 2.6 (22)% $HRe_3(CO)_{14}$, and 0.8 (14)% $Re_3(CO)_{14}$. [b] For composition of 97% $DRe_3(CO)_{14}$, 3% $HRe_3(CO)_{14}$, and 0% $Re_3(CO)_{14}$. [c] Standard deviation in parentheses. [d] Average of 11 scans.

Table III. Mass Spectral Analysis of the Parent Ion of a Calibrated Mixture of $HRe_3(CO)_{14}$ and $DRe_3(CO)_{14}$[a,b]

Mass	I(calcd)[c]	I(obsd)[d,e]	I(calcd) $-$ I(obsd)
948	2.20	2.33 (31)	−0.13
949	2.73	2.61 (35)	0.11
950	11.63	11.41 (87)	0.21
951	12.52	12.29 (108)	0.22
952	21.13	21.87 (222)	−0.75
953	20.73	21.34 (181)	−0.62
954	14.34	13.31 (137)	1.02
955	12.03	11.49 (117)	0.53
956	2.08	2.63 (173)	−0.55
957	0.46	0.66 (24)	−0.20
958	0.06	0.00 (0)	0.06
959	0.01	0.00 (0)	0.01

[a] R factor for average scan 4.4%; average R factor[d] 7.0 (66)%; average least-squares fit composition[d] 45.9 (26)% $DRe_3(CO)_{14}$, 51.8 (22)% $HRe_3(CO)_{14}$, and 2.3 (21)% $Re_3(CO)_{14}$. [b] 29.6 mg of $HRe_3(CO)_{14}$ and 30.3 mg of $DRe_3(CO)_{14}$ (97% d) ≡ 51% HRe_3-$(CO)_{14}$ and 49% $DRe_3(CO)_{14}$. [c] For composition of 46% DRe_3-$(CO)_{14}$, 52% $HRe_3(CO)_{14}$, and 2% $Re_3(CO)_{14}$. [d] Standard deviation in parentheses. [e] Average of 44 scans.

We report here, however, the facile exchange of $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ with D_2O in the presence of Florisil chromatographic adsorbent, monitored by mass spectrometry. Owing to the possibility of an isotope effect in the ionization process and the presence of random errors in the recording system, a determination of the accuracy and precision of this analytical method[4] was undertaken. Finally, as an extension of our thermal hydrogenation syntheses,[4,5] several of the compounds used in these studies have been prepared by photolytic hydrogenation of $Re_2(CO)_{10}$. A parallel and independent study of this latter reaction has already appeared.[6]

Results

Mass Spectrometric Error Analysis. In order to determine the reliability of mass spectrometrically derived isotopic compositions, we have obtained mass spectra for $HRe_3(CO)_{14}$, $DRe_3(CO)_{14}$, and a carefully prepared homogeneous mixture of the two. The average observed spectra and MASPAN[4] computer analyses for the parent ions are given in Tables I–III. These compounds were chosen because they are readily prepared (see Experimental Section), are air stable, have only one hydrogen, exhibit little or no hydrogen loss in the parent ion, and cause minimal damage to the mass spectrometer probe.

We have found that the accuracy of a mass spectral assignment can be estimated from the R factor.[4] MASPAN R factors seem to be comparable to crystallographic R factors: 2–5% indicating a very good fit, 5–10% an acceptable fit, and 10–20% a likely but not necessarily certain assignment. In some cases the fit can be improved by further refinement which

allows for the effect of hydrogen loss.[4] The reliability and precision of the fit can be determined by statistical analysis of multiple scans described as follows.

The standard deviations of the observed peaks in Tables I–III are about 7–13% of their height for those peaks which contribute more than 1% to the total multiplet intensity. The random error of an individual peak is therefore estimated to be about ±10%. This relatively large error indicates that spectral averaging is necessary for best results. The standard deviations of the least-squares fitted isotopic compositions are somewhat lower, about 2–3%. The standard deviation of the *mean* (σ_m) for the observed spectra, however, are smaller than the standard deviations listed by a factor of 1 over the square root of the number of scans (i.e., 0.29 for Table I, 0.30 for Table II, and 0.15 for Table III). It can be seen from this that the calculated and average observed spectra disagree by as much as $10\sigma_m$ in some cases. There thus appears to be a nonrandom error in these measurements. Although the 44 scans of the parent ion of the mixed sample were run under a variety of machine conditions (see Experimental Section), no significant trends in the errors or compositions were apparent. Recently, the mass spectrometer was interfaced with a PDP-11 computer. Preliminary evidence indicates that manually measured chart paper peak heights and computer-acquired integrated peak areas have roughly the same precision and give nearly equal composition analyses.

A comparison between the prepared and the mass spectrometrically determined composition of a mixture of $HRe_3(CO)_{14}$ and $DRe_3(CO)_{14}$ is given in Table III. The observed 2% $Re_3(CO)_{14}$ component of the parent ion peak was distributed equally between the two species. The accuracy of the analysis is limited by its precision since the prepared and determined compositions agree within the experimental error of ~2%: $HRe_3(CO)_{14}$, prepared 51%, determined 53%; $DRe_3(CO)_{14}$, prepared 49%, determined 47%. The isotope effect on ionization thus appears to be minimal for this compound. This is probably due to the fact that the ionized electrons are removed from orbitals which do not contain appreciable hydrogen or deuterium character. These results should hold true for most transition metal complexes, *but calibrations should be carried out wherever possible and especially for studies requiring a high degree of accuracy.*

Hydrogen–Deuterium Exchange Studies. Having established an estimated error for the analytic technique, it is possible to discuss the results of hydrogen–deuterium exchange reactions. An early indication that such isotopic exchange could take
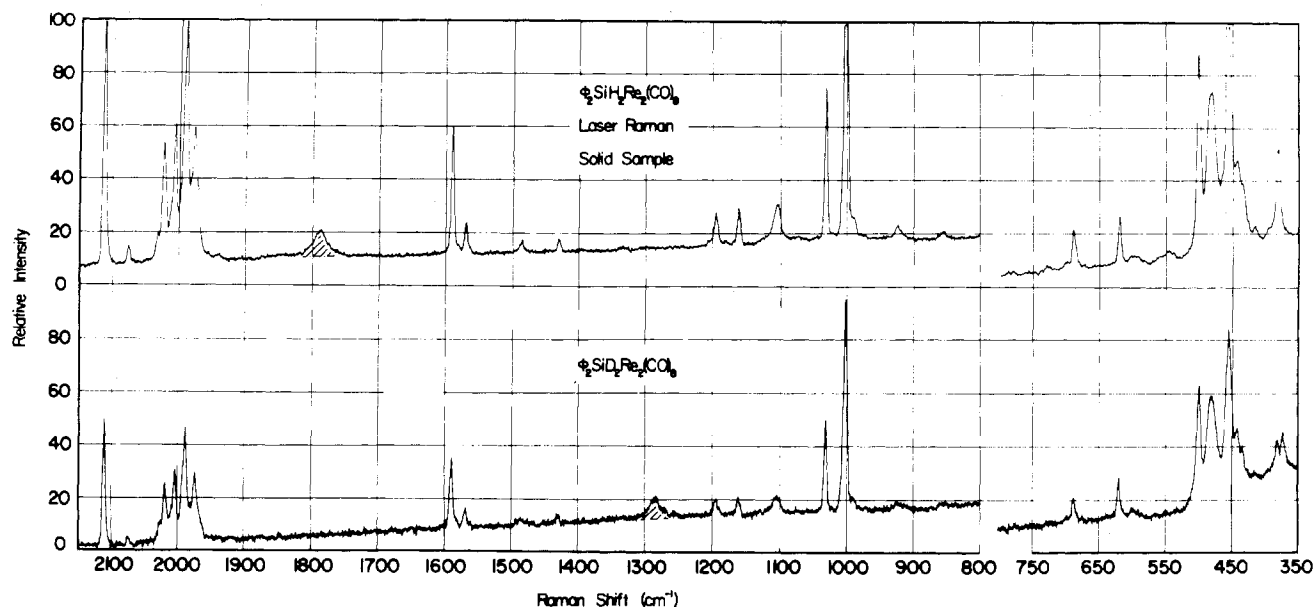
Figure 1. Raman spectra of $(C_6H_5)_2SiH_2Re_2(CO)_8$ and $(C_6H_5)_2SiD_2Re_2(CO)_8$.

Table IV. Mass Spectral Analyses of the Parent Ion of Deuterated $H_2Re_2(CO)_8$

Mass	Run 1[a,b]		Run 2[c,d]	
	I(calcd)[e]	I(obsd)[f,g]	I(calcd)[h]	I(obsd)[f,i]
596	7.21	7.19 (22)	1.63	1.64 (68)
597	5.65	5.72 (28)	5.31	4.97 (53)
598	24.72	24.99 (64)	12.12	12.15 (98)
599	18.19	18.45 (32)	16.54	16.89 (151)
600	24.02	24.05 (21)	27.21	27.49 (167)
601	15.55	15.53 (10)	15.13	15.05 (202)
602	3.83	3.82 (37)	19.46	19.71 (255)
603	0.50	0.25 (18)	1.94	1.94 (45)
604	0.07	0.00 (0)	0.38	0.15 (21)
605	0.01	0.00 (0)	0.03	0.00 (0)

[a] R factor 1.0%. [b] Average least-squares fit composition 5.5 (10)% $D_2Re_2(CO)_8$, 37.0 (0)% $HDRe_2(CO)_8$, 55.5 (17)% H_2Re_2-$(CO)_8$ + $DRe_2(CO)_8$, 1.3 (3)% $HRe_2(CO)_8$, and 0.8 (4)% $Re_2(CO)_8$. [c] R factor 1.6%. [d] Average least-squares fit composition 50.4 (72)% $D_2Re_2(CO)_8$, 35.4 (47)% $HDRe_2(CO)_8$, 12.2 (44)% $H_2Re_2(CO)_8$ + $DRe_2(CO)_8$, 1.4 (26)% $HRe_2(CO)_8$, and 0.6 (6)% $Re_2(CO)_8$. [e] For composition 6% $D_2Re_2(CO)_8$, 37% $HDRe_2(CO)_8$, 55% $H_2Re_2(CO)_8$ + $DRe_2(CO)_8$, 1% $HRe_2(CO)_8$, and 1% $Re_2(CO)_8$. [f] Standard deviation in parentheses. [g] Average of four scans. [h] For composition 50% $D_2Re_2(CO)_8$, 35% $HDRe_2(CO)_8$, 13% $H_2Re_2(CO)_8$ + $DRe_2(CO)_8$, 2% $HRe_2(CO)_8$, and 0% $Re_2(CO)_8$. [i] Average of five scans.

place was found in a Raman study carried out in our group.[7] Figure 1[8] shows the Raman spectra of $Re_2(CO)_8(SiPh_2H_2)$[9a] and $Re_2(CO)_8(SiPh_2D_2)$. These complexes each had been treated with silicic acid in chloroform to give $H_2Re_2(CO)_8$[9b] or correspondingly $D_2Re_2(CO)_8$. The Raman spectra of these products are shown in Figure 2.[8] The features identifiable as the modes of bridging hydrogen or deuterium atoms are shaded in these figures; a discussion of these is given in a separate section below. It was readily apparent that the deuterium atoms in $Ph_2SiD_2Re_2(CO)_8$ were completely retained during its preparation from Ph_2SiD_2 and $Re_2(CO)_{10}$ but that extensive H–D exchange occurred upon conversion to $D_2Re_2(CO)_8$. Similarly, a sample of "$D_2Re_2(CO)_8$" prepared photolytically from $Re_2(CO)_{10}$ and D_2 gas (see Experimental Section) but isolated by chromatography was identified mass spectroscopically as pure $H_2Re_2(CO)_8$. In contrast, the $DRe_3(CO)_{14}$ prepared in the same reaction *remained completely deuterated* (it was used in the error analysis presented in the previous section).

Table V. Mass Spectral Analyses of the Parent Ion of Deuterated $H_2Os_3(CO)_{10}$

Mass	Run 1[a,b]		Run 2[c,d]	
	I(calcd)[e]	I(obsd)[f,g]	I(calcd)[h]	I(obsd)[f,i]
844	0.12	0.00 (1)	0.02	0.00 (0)
845	0.30	0.08 (15)	0.06	0.01 (1)
846	0.82	0.38 (41)	0.20	0.14 (12)
847	1.58	1.28 (28)	0.51	0.38 (33)
848	3.29	3.07 (25)	1.16	0.86 (75)
849	4.83	4.59 (26)	2.30	1.75 (120)
850	7.89	7.71 (37)	4.04	3.81 (64)
851	9.17	9.18 (28)	6.15	6.02 (65)
852	13.43	13.63 (30)	8.69	8.73 (66)
853	11.42	11.83 (34)	10.94	11.61 (86)
854	14.77	15.32 (31)	13.09	14.18 (159)
855	9.12	9.64 (44)	12.62	13.59 (163)
856	12.97	13.89 (66)	12.87	13.88 (169)
857	2.09	1.69 (27)	10.14	10.53 (79)
858	6.80	7.25 (61)	9.05	8.99 (63)
859	0.79	0.50 (42)	3.14	2.12 (171)
860	0.60	0.05 (10)	4.43	3.22 (166)
861	0.07	0.00 (0)	0.54	0.27 (25)
862	0.01	0.00 (0)	0.11	0.00 (0)
863	0.00	0.00 (0)	0.01	0.00 (0)

[a] R factor 6.1%. [b] Average least-squares fit composition 7.3 (52)% $D_2Os_3(CO)_{10}$, 0.0 (0)% $HDOs_3(CO)_{10}$, 92.6 (67)% H_2Os_3-$(CO)_{10}$ + $DOs_3(CO)_{10}$, 0.0 (0)% $HOs_3(CO)_{10}$, and 0.0 (0)% $Os_3(CO)_{10}$. [c] R factor 8.3%. [d] Average least-squares fit composition 65.3 (58)% $D_2Os_3(CO)_{10}$, 32.5 (29)% $HDOs_3(CO)_{10}$, 2.3 (38)% $H_2Os_3(CO)_{10}$ + $DOs_3(CO)_{10}$, 0.0 (0)% $HOs_3(CO)_{10}$, and 0.0 (0)% $Os_3(CO)_{10}$. [e] For composition 7% $D_2Os_3(CO)_{10}$, 0% $HDOs_3(CO)_{10}$, 93% $H_2Os_3(CO)_{10}$ + $DOs_3(CO)_{10}$, 0% $HOs_3(CO)_{10}$. [f] Standard deviation in parentheses. [g] Average of three scans. [h] For composition 66% $D_2Os_3(CO)_{10}$, 33% $HDOs_3(CO)_{10}$, 1% $H_2Os_3(CO)_{10}$ + $DOs_3(CO)_{10}$, 0% $HOs_3(CO)_{10}$, and 0% $Os_3(CO)_{10}$. [i] Average of four scans.

A similar pair of observations was noted in our previous work[4] on the thermal treatment of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ with D_2. The former gave pure $D_4Ru_4(CO)_{12}$, but the latter yielded, after similar chromatographic separation of products, incompletely deuterated $D_2Os_3(CO)_{10}$. Initially[4] we suspected exchange of hydrogen with the hydrocarbon solvent; however, the subsequent isolation of pure $D_2Os_3(CO)_{10}$ by this reaction when followed by crystallization techniques[10] led us to suspect that exchange was occurring in our use of the chromatographic separation (with water adsorbed on the support). These
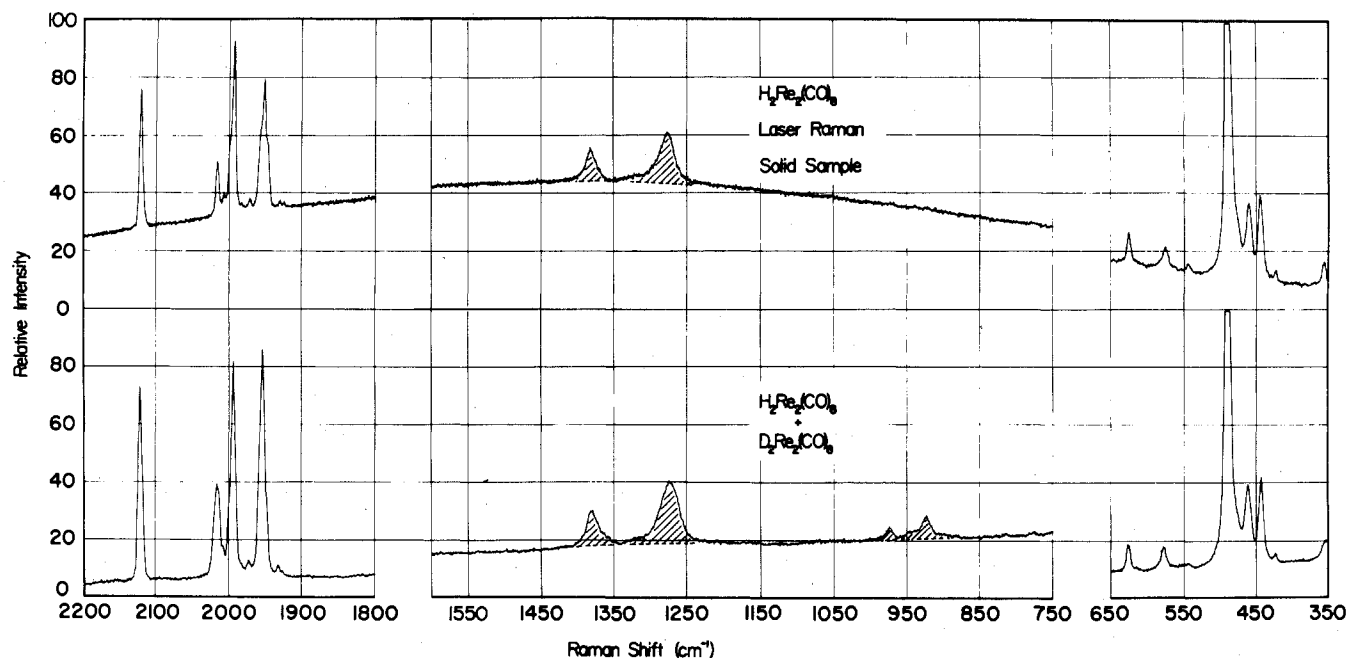
Figure 2. Raman spectra of $H_2Re_2(CO)_8$ and $D_2Re_2(CO)_8$.

suspicions were confirmed by experiment, described as follows.

$H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ were stirred with D_2O-treated Florisil and subsequently analyzed by mass spectrometry (Tables IV and V). Run 1 represents limited treatment under identical conditions (see Experimental Section). The ratio of total deuterium[11] (25% for $D_2Re_2(CO)_8$ to 7% for $D_2Os_3(CO)_{10}$) gives a lower limit of about 3.6:1 for the relative exchange rate of $H_2Re_2(CO)_8$ as compared to $H_2Os_3(CO)_{10}$. Run 2 represents more extensive treatment with unequal time periods (4 h for $H_2Re_2(CO)_8$ and 15.5 h for $H_2Os_3(CO)_{10}$). These were selected on the basis of the first runs. The total deuterium contents for run 2 were 68% for $D_2Re_2(CO)_8$ and 83% for $D_2Os_3(CO)_{10}$ (exchange rate ratio of 3.1:1, assuming deuterium is not the limiting reagent). These results are in accord with the visual observation of greater adsorption on Florisil of $H_2Re_2(CO)_8$ than of $H_2Os_3(CO)_{10}$. These results also show that it is possible to monitor the deuterium content of high molecular weight, isotopically complicated molecules by means of computerized statistical analysis of averaged spectra.

Discussion

Since both terminal[12] and bridging[1,13] hydrides are thermodynamically quite acidic, relative exchange rates could be controlled by a steric factor derived from the coordinated carbonyl groups. In terminal hydridometal complexes the hydrogen is readily accessible to assisting bases leading to rapid exchange as in $HRe(CO)_5$.[2] In the nonexchanging bridging hydrides $H_3Re_3(CO)_{12}$,[2] $H_4Ru_4(CO)_{12}$,[4] and $HRe_3(CO)_{14}$ access to the hydrogen by even a small base such as water (van der Waals diameter of 2.8–4.0 Å) is hindered by the adjacent carbonyls (idealized geometry is given in structure A).[14] The enhanced exchange rates observed for the bridging hydrogens in $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ could simply be a result of the larger carbonyl separation (structure B).[15]

There is a second important distinguishing feature in these two complexes. Both $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ are electronically unsaturated.[1] $H_4Re_4(CO)_{12}$[16] is another compound in this class, but we could not investigate its exchange properties since it decomposes in the presence of D_2O. All three of these electron-deficient complexes react rapidly with nucleophiles to give cleavage products[16,17] and/or adducts containing terminal hydrides.[17,18] This contrasts with normal


A

B
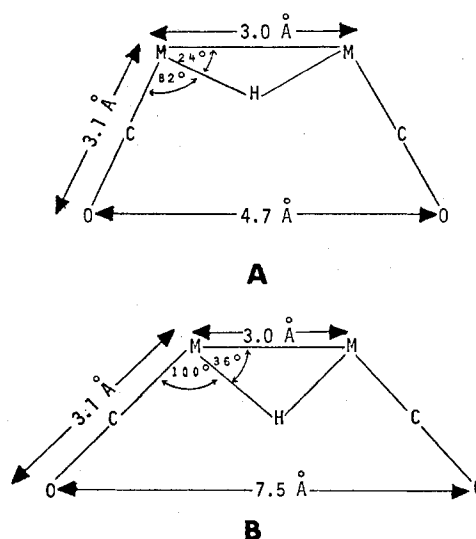
hydrogen-bridged clusters for which elevated temperatures are required for reaction with nucleophiles.[19] This suggests that the enhanced exchanged rates for $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ could be due to reactions of the type
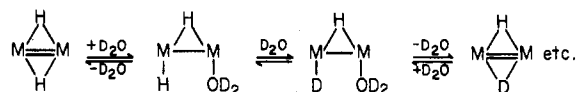
We have noted, however, that the Florisil appears to be necessary as a catalyst for the exchange.[10b] These results indicate that careful control experiments are necessary when working with deuterated metal carbonyls but also that exchange with D_2O may be a convenient method for synthesis of certain deuteriometal cluster complexes.

Bridging-Hydrogen Stretching Modes in $H_2Re_2(CO)_8$ and $Ph_2SiH_2Re_2(CO)_8$. For $H_2Re_2(CO)_8$ of D_{2h} symmetry[9c] two stretching modes for bridging hydrogen are expected in each of the Raman and IR spectra. Due to the presence of a center of symmetry in the molecule, no coincidences are expected between the Raman and IR modes. The Raman spectrum shows two bands, the shaded features in Figure 2 at 1275 and 1382 cm^{-1} for $H_2Re_2(CO)_8$ and 922 and 973 cm^{-1} for

A_g (R) B_{1g} (R) B_{2u} (IR) B_{3u} (IR)
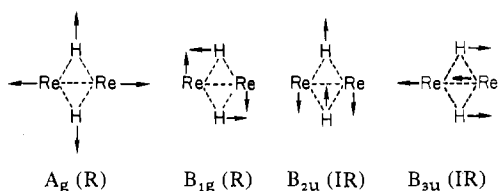
$D_2Re_2(CO)_8$. These are all somewhat broad as observed in the absorptions of other hydrogen-bridged systems.[1b] Infrared spectra of $H_2Re_2(CO)_8$ (not shown here) exhibit only one prominent feature in this region, a broad band centered at 1249 cm^{-1}. Weaker and broader features are observed near this band which cannot be assigned with any confidence at this time.

For $Ph_2SiH_2Re_2(CO)_8$ the structure but not the position of the bridging hydrogen atoms was determined by Elder.[9b] Two bands, a symmetric and an antisymmetric mode, are expected for this derivative if the motions of the bridging hydrogen atoms are significantly coupled. In most silane derivatives containing the SiH$_2$ group these two types of vibrations are so close together as to be indistinguishable.[20] It is therefore not surprising that only one band is observed in the Raman spectrum of $Ph_2SiH_2Re_2(CO)_8$, the shaded feature at 1790 cm^{-1} in the top scan of Figure 1 or at 1280 cm^{-1} in the deuteride, lower scan, Figure 1. It should also be noted that the positions of these bands are well above those observed for modes of hydrogen or deuterium bridging between two transition metal atoms[1b] and thus lend support to the assumption that the silicon is participating in the bridging system.[9a,b]

Experimental Section

Reactions and recrystallizations were carried out under nitrogen using Schlenk techniques unless otherwise indicated. Photolyses employed a Hanovia 450-W mercury lamp at a distance of about 15 cm from water-cooled Pyrex flasks.

Raman spectra were obtained on a Cary 81 spectrophotometer equipped with a Spectro-Physics 125 He/Ne laser (exciting line at 15 803 cm^{-1}); the data were obtained on microcrystalline powders held in a parabolic sample holder.

Mass Spectral Studies. Mass spectra were obtained by Ms. B. Irwin and Dr. K. Fang on an AEI MS-9 spectrometer with an ionizing voltage of 70 eV and a trap current of 270 μA using direct inlet. The source temperatures were 130–140 °C for $HRe_3(CO)_{14}$, 100 °C for $H_2Re_2(CO)_8$, and 100 °C for $H_2Os_3(CO)_{10}$. For $HRe_3(CO)_{14}$, peaks were recorded on photographic chart paper at speeds of 0.4–0.6 in./s with multiplier voltages of 1.7–3.0 kV and ion repeller voltages of –3.0 to +2.0 V. For $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ spectra were recorded electronically via an interface to the departmental PDP-11 computer. Data acquisition and processing programs by Drs. L. Levine and J. Kasper provided digitized output of peak areas. A few photographic scans were also recorded for comparison with the electronic data.

Materials. Rhenium carbonyl was used as purchased from Strem, Inc., or Pressure Chemicals; $H_4Re_4(CO)_{12}$,[5] $HFeCo_3(CO)_{12}$,[21] $H_3Re_3(CO)_{12}$,[2] and $H_2Os_3(CO)_{10}$[4] were prepared by literature methods. Deuterium gas (Liquid Carbonic) and D$_2$O had isotopic purities of >99%. Samples for the Raman spectra were supplied by Professor W. A. G. Graham and prepared as indicated above.[9]

Photolytic Hydrogenation of $Re_2(CO)_{10}$. Hydrogen gas was passed through a solution of $Re_2(CO)_{10}$ (1.0 g, 1.55 mmol) in hexane (250 mL) under UV irradiation for 1 h to give a yellow solution. The solvent and $HRe(CO)_5$ were removed under vacuum and collected in a liquid nitrogen cooled trap. The $HRe(CO)_5$ (yield estimated to be ~15–25% by conversion to $HRe(CO)_4PPh_3$) was identified by its infrared spectrum in the CO stretching region.[22] The residual solid was chromatographed on Florisil (in air). Hexane eluted a yellow band shown to be $H_2Re_2(CO)_8$ (0.4 g, 35%) by infrared spectroscopy.[9] A 3:1 mixture of hexane–CH$_2$Cl$_2$ eluted a second yellow band identified as $HRe_3(CO)_{14}$ (0.2 g, 20%) by infrared spectroscopy.[23] Both compounds could be further purified by recrystallization from CH$_2$Cl$_2$–hexane at –20 °C. Byers and Brown reported a similar

product distribution in an independent mechanistic study.[6]

When the experiment was repeated with deuterium, the infrared spectrum of the trapped solvent showed only $DRe(CO)_5$.[22] MAS-PAN–mass spectroscopic analysis of the chromatographed solids indicated that the compositions of the products were 97% DRe_3-$(CO)_{14}$–3% $HRe_3(CO)_{14}$ (Table II) and 100% $H_2Re_2(CO)_8$.

Calibrated Mixture of $HRe_3(CO)_{14}$ and $DRe_3(CO)_{14}$. Freshly recrystallized samples of $HRe_3(CO)_{14}$ (29.6 mg) and $DRe_3(CO)_{14}$ (30.3 mg) were codissolved in CH$_2$Cl$_2$–hexane and recrystallized to ensure homogeneity. The recrystallized product was analyzed by mass spectrometry (Table III).

Hydrogen–Deuterium Exchange Reactions. Run 1. Florisil (5 g) was treated with a mixture of CH$_3$OH (15 mL) and D$_2$O (5 mL) for 24 h. The solvent was removed under vacuum and the process repeated. $H_2Re_2(CO)_8$ (68 mg) was dissolved in D$_2$O-treated CH$_2$Cl$_2$ (20 mL) and treated with a 2.5-g aliquot of the Florisil for 2 h and 45 min. $H_2Os_3(CO)_{10}$ (40 mg) was treated similarly. The solutions were then syringed away from the Florisil with 2 × 5 mL washes and the solvent was evaporated. The solids were then analyzed by mass spectrometry (Tables IV and V).

Run 2. Florisil (7.5 g) was treated with D$_2$O (10 mL) for 3 days. The excess D$_2$O was removed under vacuum and the Florisil divided into three equal parts. One part was stirred with $H_2Re_2(CO)_8$ (34 mg) and D$_2$O-treated hexane (40 mL) for 4 h. A second was stirred with $H_2Os_3(CO)_{10}$ (35 mg) and D$_2$O-treated hexane (40 mL) for 15.5 h. The third was stirred with $HFeCo_3(CO)_{12}$ (40 mg) for 3 h during which time the purple solution became colorless and the Florisil changed from purple to brown indicating decomposition had occurred. A solution of $H_4Re_4(CO)_{12}$ in CH$_2$Cl$_2$ treated with D$_2$O without Florisil also decomposed as evidenced by a color change from deep red-brown to yellow. The $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ solutions were syringed away from the Florisil with 2 × 5 mL washes and the solvent was evaporated. The solids were then analyzed by mass spectrometry (Tables IV, V).

A solution of $H_2Re_2(CO)_8$ in CH$_2$Cl$_2$ treated for 4 h with D$_2$O alone showed essentially no deuterium incorporation.

Registry No. $HRe_3(CO)_{14}$, 12086-80-5; $DRe_3(CO)_{14}$, 62107-55-5; $H_2Re_2(CO)_8$, 38887-05-7; $H_2Os_3(CO)_{10}$, 41766-80-7; $(C_6H_5)_2Si$-$H_2Re_2(CO)_8$, 25776-56-1; $(C_6H_5)_2SiD_2Re_2(CO)_8$, 62107-56-6; $D_2Re_2(CO)_8$, 62066-82-4.

Supplementary Material Available: Tables listing the frequencies of the Raman bands shown in Figures 1 and 2 (3 pages). Ordering information is given on any current masthead page.

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(8) Tables listing the frequencies of the Raman bands shown in Figures 1 and 2 are available as supplementary material.
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of $D_2Os_3(CO)_{10}$ on silica gel but that direct exchange with D_2O or C_6H_5OD does not occur in the absence of silica; extended interaction of $H_2Os_3(CO)_{10}$ with H_2O in acetone gives $HOs_3(CO)_{10}(OH)$.

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(17) $H_2Re_2(CO)_8$ reacts with PPh_3 in hexane at room temperature in 10 min to give an adduct (ν_{CO} 2104 (w), 2073 (w), 2022 (sh), 2014 (m), 2008 (s), 1980 (m), 1967 (m) and 1949 (m) cm^{-1} (cyclohexane solution) presumed to be $HRe(CO)_4(\mu\text{-}H)Re(CO)_4PPh_3$. Attempts to obtain NMR spectra in benzene resulted in decomposition to $HRe(CO)_4PPh_3$: M. A. Andrews and H. D. Kaesz, unpublished observations.
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## Coupled Electron- and Proton-Transfer Equilibria in Some Iron–Oxime and Related Systems

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Loss of an electron from a complexed metal ion will in general augment the acidity of dissociable protons present on the ligand frame. When the metal–ligand combination is right, oxidation and deprotonation may occur in a coupled manner. The occurrence of such coupled reactions has been postulated in metal ion catalyzed bioreactions.[1] In this work examples of coupled electron and proton reactions are revealed in a variable-pH cyclic voltammetric (CV) study of the low-spin pseudooctahedral iron(II) species[2,3] $Fe(H_2RR'L)^{2+}$, **1**, which
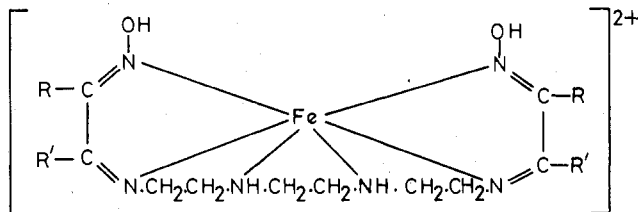
1

has two dissociable oxime protons.

Experimental Section

A. Preparation of Compounds. The synthesis of $Fe(H_2Me_2L)(ClO_4)_2$ was described earlier.[2] $Fe(H_2EtMeL)(ClO_4)_2$ was similarly prepared in 70% yield by reacting ferrous sulfate heptahydrate with H_2EtMeL.[2] Anal. Calcd for $C_{16}H_{32}N_6O_{16}Cl_2Fe$: C, 32.26; H, 5.42; N, 14.12; Fe, 9.38. Found: C, 32.24; H, 5.72; N, 14.10; Fe, 9.20. $Fe(H_2MeEtL)(ClO_4)_2$ was prepared as follows. A 0.49-g sample (0.0033 mol) of triethylenetetramine was added to an ethanolic solution of 0.77 g (0.0066 mol) of isonitrosoethyl ethyl ketone.[2] An ethanolic solution of 1.21 g (0.0033 mol) of iron(II) perchlorate hexahydrate
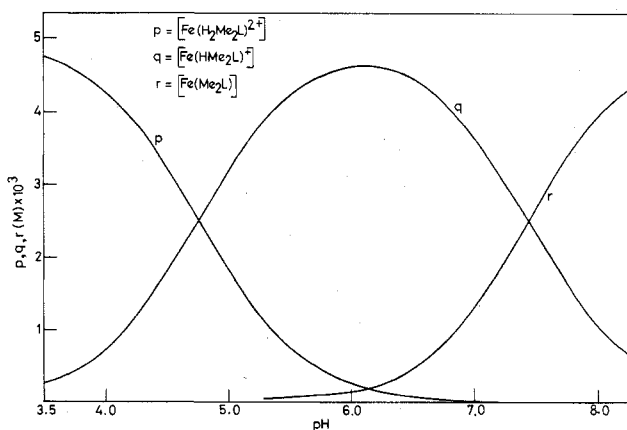

Figure 1. Formation curves of iron(II) species.

was added to the above mixture. The mixture was heated to reflux for 4–5 h with constant stirring. Deep violet crystals deposited in 50% yield. Those were filtered off and were washed with alcohol followed by ether. Anal. Calcd for $C_{16}H_{32}N_6O_{16}Cl_2Fe$: C, 32.26; H, 5.42; N, 14.12; Fe, 9.38. Found: C, 32.14; H, 5.81; N, 14.20; Fe, 9.10. All complexes are indefinitely stable at room temperature.

Like $Fe(H_2Me_2L)(ClO_4)_2$ both $Fe(H_2EtMeL)(ClO_4)_2$ and $Fe(H_2MeEtL)(ClO_4)_2$ are diamagnetic. Their electronic and IR spectra[2] are very similar.

B. pH-metric Titrations. These were done on 40 mL of 0.005 M $Fe(H_2Me_2L)(ClO_4)_2$ with carbonate-free sodium hydroxide solution (0.01 N) at 298 K. Further experimental details and also details concerning treatment of data for obtaining K_1 and K_2 and formation curves are delineated elsewhere.[4]

C. Cyclic Voltammetry and Constant-Potential Coulometry. These were performed in an instrument fabricated in this laboratory, in the same manner as described elsewhere.[4]

Results and Discussion

A. Dissociation of Oxime Protons. The complex $Fe(H_2Me_2L)^{2+}$ was titrated pH-metrically with alkali. From the titration data, the stepwise acid dissociation constants pK_1 and pK_2 corresponding to

$$Fe(H_2RR'L)^{2+} \xrightleftharpoons{K_1} Fe(HRR'L)^+ + H^+ \tag{1}$$

$$Fe(HRR'L)^+ \xrightleftharpoons{K_2} Fe(RR'L) + H^+ \tag{2}$$
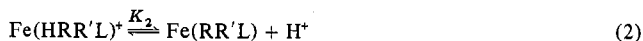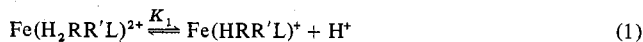
were found to be (298 K) 4.75 ± 0.05 and 7.45 ± 0.05, respectively. The formation curves (Figure 1) were constructed using these equilibrium constants. Up to pH 4, $Fe(H_2Me_2L)^{2+}$ alone makes the major contribution to the solution composition while at pH 8.2 the major species is $Fe(Me_2L)$. The intermediate species $Fe(HMe_2L)^+$ is most important in the narrow pH range 5.6–6.6.

B. Cyclic Voltammetric Results. The case of $Fe(H_2Me_2L)(ClO_4)_2$ will be described first (Table I and Figure 2). *All potentials are referenced to the saturated calomel electrode (SCE).* The peak separation (ΔE_p) remains close to 60 mV in the entire range of pH (1.55–8.90) and scan rates (0.012–0.213 V s^{-1}) studied (Table I). Evidently it is a reversible one-electron transfer.[5] The one-electron involvement is fully corroborated by constant-potential (oxidation at 0.45 V at room temperature) coulometry in acetate buffer at pH 3.25: 1.14×10^{-5} mol of $Fe(H_2Me_2L)(ClO_4)_2$ in 250 mL of buffer was electrolyzed to complete the oxidation. Amount of electricity consumed was 1.14 C (calculated value 1.10 C).

While ΔE_p remains invariant, the peak potentials and hence their average ($\bar{E}_p$) shift considerably with pH until pH 8.20 is reached. This pH dependence means that protons are involved in the electrode process. For the general reversible reaction in well-buffered media

$$Ox + ne^- + mH^+ \rightleftharpoons H_mRed \tag{3}$$