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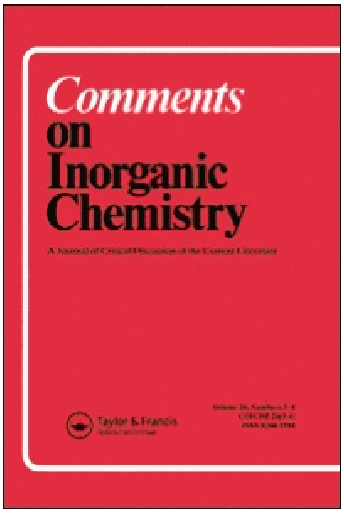

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Nitrosyl Substituted Hydride Complexes-An Activated Class of Compounds

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Nitrosyl Substituted Hydride Complexes—An Activated Class of Compounds

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The activation of metal hydrogen bonds toward alkyne insertion and carbonyl reduction in NO substituted transition metal hydride complexes is discussed. MO theoretical treatment elucidates a genuine nitrosyl effect and enhanced hydricity for this class of compounds. This is traced in NMR based M–H bond ionicity measurements and reactivity studies.

Key Words: *metal hydrides, metal nitrosyl hydride complexes, alkyne insertion, hydride transfer, carbonyl reduction, metal hydrogen bond ionicity*

Abbreviations Used: Cp = η^5-C_5H_5, py = pyridine

INTRODUCTION

Recently there has been increasing interest in the chemistry of NO stimulated by the discovery of its unique biochemical role as a neurotransmitter.[1] Mainly for this reason it has been elected molecule of the year 1992.[2] In this regard it is also noteworthy that transition metal complexes are believed to be part of the metabolism. Its uniqueness is, however, not restricted to biochemistry, and the propensity of the NO ligand to lead to unusual structural

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and electronic effects in the corresponding complexes has been well recognized in coordination chemistry.[3]

Textbooks usually treat the NO molecule as a linearly coordinated three electron donating ligand which then possesses strong π accepting properties. In rarer instances, however, NO can also act as a one electron donor with a bent MNO unit.[4] This corresponds to a formal Lewis base description of NO as $N{\equiv}O^+$ (linear) and $N{=}O^-$ (bent) and demonstrates the "non-innocent" ligand behaviour of NO. The latter change in electronic nature in the linear and bent binding mode, together with the strong π accepting power of the most widespread linear coordination of NO, can be used to explain the majority of the unusual structural and reactivity properties in transition metal nitrosyl complexes.

A closer inspection of the electronic properties elucidates an extended scope of nitrogen monoxide's ligand capabilities. It is the intention of this paper to focus on these specific aspects with regard to the binding and reactivity of the hydrogen ligand (H, H_2) in the coordination sphere of transition metal complexes. Our research has been involved in the investigation of the influence of phosphorus and nitrosyl donor ligands on the character of transition metal hydrogen bonds ($L_nM{-}H$) for which ligand induced enhanced "hydridicity" of the H ligand was expected and indeed observed.

This account is organized as follows: After a descriptive survey of the known nitrosyl hydride complexes, the theoretical background of ligand binding in these compounds will be discussed in some detail and will provide an explanation for the unique physical properties, particularly the polar character of the M–H bond in these complexes. Consequences thereof with respect to reactivity with emphasis on insertion chemistry of these species will be a special topic of this review.

SURVEY OF TRANSITION METAL NITROSYL HYDRIDE COMPLEXES

Table I represents an overview of the presently known transition metal nitrosyl hydride compounds and includes selected spectroscopic data. Their syntheses have been reviewed in detail elsewhere[3,5] and will not be repeated here.

It is interesting to note that nitrosyl hydride members of the

TABLE I

Selected ^{1}H NMR and IR data for transition metal nitrosyl hydrides.

Compound	^{1}H NMR	IR		Ref.
	δ(H)/J(MH)/J[PH]	ν(MH)(ν(MD))	ν(NO)(MD isotopomer)	
Group 6: Cr/Mo/W				
$Cr(CO)_4(NO)H$	-4.85		1740	6
$Cr(CO)_2(NO)(PEt_3)_2H$	-5.67[36.6]	1661		7
$Cr(CO)_2(NO)(PMe_3)_2H$	-5.46[41.0]	1650		7
$Cr(CO)_2(NO)(PPh_3)_2H$	-3.51[32.7]	1668	1638	7
$Cr(CO)_2(NO)[P(OMe)_3]_2H$	-5.32[53.7]	1690	1664	7
$Cr(CO)_2(NO)[P(OPh)_3]_2H$	-5.35[56.5]	1714	1685	7
$MoCp(NO)_2H$		1805	1642,1732	8
$Mo(NO)(dppe)_2H$			1545	9
$WCp(NO)_2H$	2.77	1900(1372)	1632,1718	8
$[Cp_2Co][CpW(NO)_2H)]$	radical	1848	1445(1447) 1521(1513)	10
$W(NO)(dppe)_2H$			1535	11
$W(CO)_2(NO)(PEt_3)_2H$	-1.84(30.0)	1671	1592(1622)	11
$W(CO)_2(NO)(PMe_3)_2H$	-1.27(30.7)	1665	1590(1627)	11
$W(CO)_2(NO)(PPh_3)_2H$	0.64(31.4)	1681	1596(1629)	12
$W(CO)_2(NO)[P(OiPr)_3]_2H$	-1.18(27.9)	1702	1613(1637)	11
$W(CO)_2(NO)[P(OMe)_3]_2H$	-1.59(26.7)	1702	1619(1646)	11
$W(CO)_2(NO)[P(OPh)_3]_2H$	-1.14(25.1)	1721	1638	11
$WCp(NO)I[P(OPh)_3]H$	-2.04(54)	1883	1643	13, 14
$WCp(NO)I[P(OMe)_3]H$	-1.44(57)	1923	1629	13
$WCp(NO)I(PPh)_3H$	0.31(58)		1615	13
$WCp(NO)I(PMe_3)H$ (isomer A)	-0.65(66)	1931	1613	13
$WCp(NO)[P(OPh)_3]H_2$	-1.82(88)	1863	1607	13
$WCp(NO)[P(OMe)_3]H_2$	-1.74(87)			13
$WCp(NO)(CH_2SiMe_3)[P(OPh)_3]H$				14
$WCp(NO)(CH_2SiMe_3)[P(MePh_2)H$				14
$WC_5Me_5(NO)(CH_2SiMe_3)(PMe_3)H$	-1.25		1545	14
Group 7: Mn/Tc/Re				
$Mn(C_5H_4Me)(NO)(PPh_3)H$	-6.48[88.8]		1683	15
$Mn(NO)_2(PMe_3)_2H$	-0.10[107.5]		1683,1637	16
$Mn(NO)_2(PEt_3)_2H$	-0.49[101.1]		1675,1633	16
$Mn(NO)_2(PPh_3)_2H$				17
$Mn(NO)_2[P(OMe)_3]_2H$	-0.60[95.7]		1720,1667	16

TABLE I (*Continued*)

Compound	^1H NMR	IR		Ref.
	δ(H)/J(MH)/J[PH]	ν(MH)(ν(MD))	ν(NO)(MD isotopomer)	
$Mn(NO)_2[P(OEt)_3]_2H$	-0.23[96.4]		1706,1661	16
$Mn(NO)_2[P(OiPr)_3]_2H$	-0.13[95.6]		1699,1655	16
$Tc(NO)(PPh_3)_3H_2$	-1.5, -3.45	1733, 1158 (1358, 801)	1636(1659)	18
$ReCp(CO)(NO)H$	-8.50		1723	19
$ReCp(PPh_3)(NO)H$	-9.15[29.7]	1982	1620	20
$Re(NO)_2(PPh_3)_2H$		1780	1580,1620	21
$Re(CO)(NO)[P(OMe)_3]_2H_2$	-5.26[32.9],-2.04[30.9]	1840	1681	22a
$Re(CO)(NO)[P(OiPr)_3]_2H_2$	-4.78[31.7],-1.51[30.2]	1850	1671	22a
$Re(CO)(NO)(PMe_3)_2H_2$	-4.24[28.1],-0.81[27.0]	1803	1655	22a
$Re(CO)(NO)(PEt_3)_2H_2$	-5.1[26.1],-1.42[26.4]	1809	1652	22a
$Re(CO)(NO)(PiPr_3)_2H_2$	-5.37[23.7],-1.35[26.2]		1650	22a
$Re(CO)(NO)(PCy_3)_2H_2$	-4.9[24.0],-1.0[26.0]		1623	22a
$Re(NO)(PPh_3)_3H_2$	-0.9[30],-2.1[30]	1800,1950	1640	22b
$ReCl(CO)(NO)[P(OMe)_3]_2H$	1.75[28.8]	1844	1701	22a
$ReCl(CO)(NO)[P(OiPr)_3]_2H$	2.22[28.6]	1845	1693	22a
$ReCl(CO)(NO)(PMe_3)_2H$	1.68[24.4]	1811	1668	22a
$ReCl(CO)(NO)(PEt_3)_2H$	1.50[22.3]	1827	1669	22a
$ReCl(CO)(NO)(PiPr_3)_2H$	1.57[22.2]		1671	22a
$ReF(CO)(NO)(PPh_3)_2H$	4.73[22.6]	1835(1284)	1662(1675)	23
$Re(OMe)(CO)(NO)(PPh_3)_2H$	3.82[22.9]	1871(1343)	1671(1670)	24
$Re(OEt)(CO)(NO)(PPh_3)_2H$	3.83[23.1]	1868	1669	24
$[Re(CO)(NO)(PPh_3)_3H]ClO_4$	1.11[32.3,18.6]	1908	1728	24
$Re(MeOH \cdot OClO_3)(CO)(NO)(PPh_3)_2H$	4.72[21.9]	1902	1738	24
$Re(EtOH \cdot OClO_3)(CO)(NO)(PPh_3)_2H$	4.63[21.4]	1900	1720	24
$Re(CO)(NO)(PPh_3)_2H_2$	0.09[26.8],-3.09[26.1]	1818,1866	1669	24
$[Re(MeOH)(NO)(PPh_3)_3H]ClO_4$	1.6	1993	1700	25
$Re(OMe)(NO)(PPh_3)_3H$		1980	1634	25
$ReF(NO)(PPh_3)_3H$		1957	1655	25
$ReCl(NO)(PPh_3)_3H$	0.79[27.5,71.4]	2017	1664,1656,1651	25
$ReBr(NO)(PPh_3)_3H$	0.47[27.8,67.8]	2020	1665,1656,1651	25
$Re(N_3)(NO)(PPh_3)_3H$	0.50[26.5,66.8]	1980	1660	25
$Re(NCO)(NO)(PPh_3)_3H$		1956	1661,1657	25
$ReF(CO)(NO)(PPh_3)_2H$	4.62[23.5]		1698	25
$ReCl(CO)(NO)(PPh_3)_2H$	3.38[23.5]		1715,1710,1704	25
$ReBr(CO)(NO)(PPh_3)_2H$	2.74[23.6]		1717,1709,1702	25
$Re(N_3)(CO)(NO)(PPh_3)_2H$	3.35[22.6]		1704,1700	25
$Re(NCO)(CO)(NO)(PPh_3)_2H$	2.90[23.0]		1702	25
$ReI(CO)(NO)(PPh_3)_2H$	1.56[23.4]		1719	25
$Re(SCN)(CO)(NO)(PPh_3)_2H$	2.34[21.5]		1726	25

TABLE I (*Continued*)

Compound	^{1}H NMR	IR		Ref.
	δ(H)/J(MH)/J(PH)	ν(MH)(ν(MD))	ν(NO)(MD isotopomer)	
$Re(OMe)(C_7H_7NC)(NO)(PPh_3)_2H$	2.95[21.4]	1864	1646	25
$ReF(C_7H_7NC)(NO)(PPh_3)_2H$	3.78[22.2]	1846	1656	25
$ReCl(C_7H_7NC)(NO)(PPh_3)_2H$	2.63[21.9]	1864	1668	25
$ReBr(C_7H_7NC)(NO)(PPh_3)_2H$	2.06[20.6]	1866	1667	25
$Re(N_3)(C_7H_7NC)(NO)(PPh_3)_2H$	2.64[21.5]	1859	1675	25
$Re(NCO)(C_7H_7NC)(NO)(PPh_3)_2H$	2.13[21.3]	1870	1679	25
$Re(I)(C_7H_7NC)(NO)(PPh_3)_2H$	1.02[21.5]	1868	1676	25
$Re(SCN)(C_7H_7NC)(NO)(PPh_3)_2H$	1.49[19.3]	1921	1686	25
$ReC_5Me_5(CO)(NO)H$	-7.59		1699	26
$[\{ReC_5Me_5(CO)(NO)\}_2\mu\text{-}H]^+$	-13.54			26
(2 isomers)	-12.33			
$[ReCp(CO)(NO)(PPh_3)(GePh_3)H]^+$	-1.58		1760	27
Group 8: Fe/Ru/Os				
$Fe(CO)_3(NO)H$				28
$Fe(CO)_2(NO)(PPh_3)H$	-3.5[12]		1755	29
$Fe(CO)(NO)(PPh_3)_2H$	-5.0[79]		1690	29
$Fe(CO)(NO)(PEt_3)_2H$	-6.65[58.6]		1709	30
$Fe(CO)(NO)(PMe_3)_2H$	-6.04[81.4]		1683	30
$Fe(CO)(NO)[P(OiPr)_3]_2H$	-6.70[75.5]		1693	30
$Fe(NO)(PF_3)_3H$	-5.87[23.3]	1900(1370)	1839	31
$Ru(NO)(PPh_3)_3H$	-6.6[30]	1970	1640	32,33, 34a
$Ru(NO)(PMePh_2)_3H$	-5.0[0]	1900	1615	32
$Ru(NO)(PiPrPh_2)_3H$	-7.2[20]	1975,1990	1600	32
$Ru(NO)(PCyPh_2)_3H$	-7.4[24]	1960,1985	1600	32
$Ru(O_2CCF_3)_2(NO)(PPh_3)_2H$	-3.8[15.9]			34
$Os(NO)(PPh_3)_3H$	-7.3[35]	2050	1620	32,34a
$Os(NO)(PMePh_2)_3H$	-6.5[7]	1970	1595	32
$Os(O_2CCF_3)_2(NO)(PPh_3)_2H$	-5.41[14.0]	2156	1820	34a
$Os(O_2CC_2F_5)_2(NO)(PPh_3)_2H$	-6.68[14.0]	2160	1817	34a
$[Os(NO)(PPh_3)_3H_2][H(O_2CCF_3)_2]$	-3.98[18.5,15.5]	2010,2100	1770	34a
	-4.25[16.0,41.0]			
$[Os(NO)(PPh_3)_3H_2]BPh_4$	-3.99[18.5,15.5]	1990,2095	1755	34a
	-4.23[16.0,41.0]			
$[Os(CO)(NO)(PCy_3)_2H_2]BPh_4$	-4.79[18.0]-7.1[22.0]		1809	34a
$Os(CO)_2(NO)(PPh_3)_2H$	-5.04[24]		1630	34b
$OsCl(NO)(PiPr_3)_2H_2$	-2.16[14.3]-10.03[23.4]	2130,2050	1713	35
$OsCl_2(NO)(PiPr_3)_2H$	-5.40[14.5]	2160	1780	35
$OsCl(CF_3COO)(NO)(PiPr_3)_2H$	-7.83[15.0]	2205	1805	35

TABLE I (*Continued*)

Compound	^{1}H NMR δ(H)/J(MH)/J[PH]	IR ν(MH)(ν(MD))	 ν(NO)(MD isotopomer)	Ref.
$OsCl(OCH_3)(NO)(PiPr_3)_2H$	-6.04[14.5]	2098	1750	35
$OsCl(C_2Ph)(NO)(PiPr_3)_2H$	0.72[23.5]	2205	1795	35
$OsCl(C_2CO_2CH_3)(NO)(PiPr_3)_2H$	-0.73[22.7]	2095	1748	35
Group 9 Co/Rh/Ir				
$[Ir(NO)(PPh_3)_3H]ClO_4$ (green isomer)		2070	1715	36
$[Ir(NO)(PPh_3)_3H]ClO_4$ (brown isomer)		2130	1720	36
$[Ir(NO)(PPh_3)_3H]ClO_4$ (black isomer)		2150	1780	36
$[Ir(NO)(PPh_3)_3H]BF_4$ (green isomer)		2070	1715	36
$[Ir(NO)(PPh_3)_3H]BF_4$ (brown isomer)		2130	1720	36
$[Ir(NO)(PPh_3)_3H]PF_6$ (green isomer)		2070	1715	36
$[Ir(NO)(PPh_3)_3H]PF_6$ (brown isomer)		2130	1720	36
$IrCl(NO)(PPh_3)_2H$		2080	1545	36
$IrBr(NO)(PPh_3)_2H$		2080	1545	36
$IrI(NO)(PPh_3)_2H$		2080	1550	36
$[Ir(NO)(AsPh_3)_3H]ClO_4$			1720	37
Bridging hydrides:				
$[CpMo(NO)_2(\mu\text{-}H)MoCp(NO)_2]BF_4$			1675,1783	38
$[CpMo(NO)_2(\mu\text{-}H)WCp(NO)_2]BF_4$	-8.92(123.6)		1650-1790(6x)	38
$[CpW(NO)_2(\mu\text{-}H)WCp(NO)_2]BF_4$	-8.33(114.2)		1660-1775(4x)	38
$[CpW(NO)_2(\mu\text{-}H)WCp(NO)_2]PF_6$			1685,1752	38
$[CpW(NO)_2(\mu\text{-}H)Cr(CO)_5]$				38
$[CpW(NO)I]_2(\mu\text{-}H)_2$	-1.21(70.8,88.3)		1646	13
$[CpW(NO)H]_2(\mu\text{-}H)_2$ (2 isomers)	6.99(95),-2.05(93) 6.55(99),1.39(92), -5.94(96)	1906	1599	13
$[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2$	1.32(151)[24]		1578	13
$[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2$	0.84(54)[26]			13
$(CO)_5W(\mu\text{-}H)W(CO)_4(NO)$	-11.77		1735	39
$(CO)_5W(\mu\text{-}H)W(CO)_3[P(OMe)_3](NO)$	-12.50(39.5)[27.0]		1693	40
$(CO)_5W(\mu\text{-}H)W(CO)_2(tBuNC)_2(NO)$	-12.6(32,43)		1648	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(tBuNC)_2(NO)$	-9.56(42,50)		1682	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(MeNC)_2(NO)$	-12.6(32,43)		1651	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(MeNC)_2(NO)$	-9.49(44,53)		1688	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(BzNC)_2(NO)$	-12.3(34,43)		1655	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(BzNC)_2(NO)$	-9.46(41,54)		1685	41
$(CO)_5W(\mu\text{-}H)W(CO)_2(THF)_2(NO)$	-5.21(50,60)		1662	41
$(CO)_5W(\mu\text{-}H)W(CO)_3(NO)(PHPh_2)$	-11.70(38.4,42.8)[21.4]		1701	42a
$(CO)_5W(\mu\text{-}H)W(CO)_3(NO)(PPh_3)$	-10.86(40.6,45.0)[17.0]		1707	42a

TABLE I (*Continued*)

Compound	^{1}H NMR	IR		Ref.
	δ(H)/J(MH)/J(PH)	ν(MH)(ν(MD))	ν(NO)(MD isotopomer)	
$(CO)_5W(\mu\text{-}H)W(CO)_3(NO)(PCy_3)$	-11.80(40.3,45.8)[14.9]		1698	42a
$(CO)_5W(\mu\text{-}H)W(CO)_3(NO)(dppf)$	-11.13(44.2,45.0)[6.6]		1701	42a
$(CO)_5W(\mu\text{-}H)W(CO)_2(NO)(PHPh_2)_2$	-11.62(36.6,42.8)[17.8]		1676	42a
$(CO)_5W(\mu\text{-}H)W(CO)_2(NO)(PPh_3)_2$	-11.40(40.0,45.1)[11.4]		1672	42a
$(CO)_5W(\mu\text{-}H)W(CO)_2(NO)(dppm)$	-10.79(38.0,40.8)[16.8]		1685	42a
$(CO)_5W(\mu\text{-}H)W(CO)_2(NO)(dppe)$	-11.73(38.0,48.0)[16.8]		1680	42a
$[(CO)_5W(\mu\text{-}H)W(CO)_3(NO)]_2(\mu\text{–}dppf)$	-11.26(40.0,44.0)[18.0]		1701	42a
$[(CO)_5W(\mu\text{-}H)W(CO)_3(NO)]_2(\mu\text{–}dppe)$	-11.40(40.5,45.0)[6.6]		1692	42a
$(OC)_5W(\mu\text{-}H)(W(CO)_3(NO)(P(p\text{-}C_6H_4Me)_3)$	-11.0(45.2,40.9)[16.9]		1700	42b
(2 isomers)	-7.93(61.0,44.4)[17.9]			
$(OC)_5W(\mu\text{-}H)(W(CO)_3(NO)(P(p\text{-}$	-11.0(44.6,40.3)[17.2]		1700	42b
$C_6H_4OMe)_3)$	-7.92(62.4,42.0)[18.0]			
2 isomers)				
$(OC)_5W(\mu\text{-}H)(W(CO)_3(NO)(P(p\text{-}C_6H_4F)_3)$	-11.0(44.6,40.5)[17.6]		1701	42b
(2 isomers)	-7.99(62.0,41.3)[17.9]			
$(OC)_5W(\mu\text{-}H)(W(CO)_3(NO)(ASPh_3)$	-11.0(44.6,40.7)		1700	42b
$[(OC)_5W(\mu\text{-}H)(W(CO)_2(NO)(\eta^2\text{-}$	-9.69(48.7,30.3)		1609	42b
$S_2CNEt_2)]NMe_4$				
$(OC)_5W(\mu\text{-}H)(W(CO)_3(NO)(py)_2$	-7.10(52.0,42.1)		1609	42b
(2 isomers)	-5.12(57.1,50.0)			
$(OC)_5W(\mu\text{-}H)(W(CO)_2(NO)(bipy)$	-9.45(47.7,36.6)		1649	42b
(2 isomers)	-7.10(53.4,46.3)			
$(OC)_5W(\mu\text{-}H)(W(CO)_2(NO)(P(p\text{-}$	-9.66(50.6,39.8)[11.4]		1662	42b
$C_6H_4Me)_3)_2$				
$(OC)_5W(\mu\text{-}H)(W(CO)_2(NO)(P(p\text{-}$	-9.59(50.4,39.8)[11.4]		1665	42b
$C_6H_4OMe)_3)_2$				
$(OC)_5W(\mu\text{-}H)(W(CO)_2(NO)(P(p\text{-}C_6H_4F)_3)_2$	-9.74(49.8,40.2)[17.6]		1662	42b
$Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NO)$	-11.85		1550	43
$Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}NO)(PPh_3)$	-11.23			43
$Ru_3(CO)_8(\mu\text{-}H)(\mu\text{-}NO)(PPh_3)_2$	-10.25			43
$Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}NO)(PPh_3)_3$	-9.63			43
$Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}NO)[P(OMe)_3]_3$	-11.86		1460	43
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NO)$			1586	43
$Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}NO)[P(OMe)_3]$			1460	43
$Os_4(CO)_{12}(\mu\text{-}H)_3(\mu\text{-}NO)$	-14.89,-17.95		1630	44

early and late transition metal series are missing. Since there is no apparent reason for this finding, it is likely that either synthetic access to this class of molecules has so far not been developed or that, alternatively, however less likely, such complexes are inherently unstable.

Table I shows that the majority of transition metal nitrosyl hydride complexes have second and third row metal centers combined with the ubiquitous cyclopentadienyl, phosphorus donor and CO ligands. While most of the mononuclear compounds are pseudooctahedral with a d^6 electron configuration, only a few have d^8 metal centers with a pentacoordinated ligand framework. Among the pentacoordinate species of the late transition metals, Ir complexes with bent NO moieties have been observed. This has been attributed to the presence of π donor ligands, such as halides, in these compounds.[5a,45] The formation of unusually stable, formally 19 electron derivatives has been reported for the one electron reduction of dinitrosyl hydride complexes.[10] Although these species are presumably better described using Tyler's $18+\delta$ electron configuration formalism,[46] i.e., with a mostly ligand based SOMO, this supplements the series of unusual chemical phenomena among nitrosyl compounds.

Among the polynuclear complexes there is a prominent subclass of bimetallic bridged hydrido tungsten compounds of the type, $(CO)_5W(\mu\text{-}H)W(CO)_2(NO)L_2$. Inspection of their structures reveals that these bimetallic compounds may be envisaged as "$W(CO)_5$" adducts of $WH(CO)_2(NO)L_2$ complexes, which have a weak metal/metal interaction based on the metal/metal distance. The latter nitrosyl hydride complexes form themselves a subclass within the monometallic section of Table I and are stable molecules with considerable Lewis basicity.

THEORETICAL ASPECTS OF NITROSYL HYDRIDE COMPLEXES

The nitrosyl ligand plays an important role within coordination chemistry. Rather than the obvious difference in ligand electron count, 3 for NO vs. 2 for CO, there may appear no clear difference between the carbon monoxide ligand and NO in the linear binding mode at first glance. Although the π accepting capabilities of NO are certainly enhanced due to the lower energy of the π^* orbitals and the filled σ donor orbital is also at slightly lower energy, this would merely explain the characteristic properties of transition metal nitrosyl complexes. Hence, the difference has to be attributed to the third and odd electron which is accommodated in the

π^* orbital of the free NO molecule. It is just this electron that is transferred to the metal center with concomitant formal reduction of it, i.e., compared to the analogous isoelectronic complexes with carbon monoxide ligands, nitrosyl complexes have metal centers with a lower formal oxidation state. This is best exemplified for the two well known hydride complexes $Mn(CO)_3L_2H$ and $Mn(NO)_2L_2H$ (L = phosphorus donor). Both have a stable 18 electron configuration; in the pseudooctahedral compounds, however, the Mn center has a d^6 electron configuration and is formally Mn(I), while in the pseudotrigonal bipyramidal nitrosyl derivatives, the metal center is formally reduced and d^8 Mn(−I). As a consequence, different ligand binding energetics and bond polarities might be expected. In the following we will analyze the electronic structure in these complexes in more detail with an emphasis on the enhanced metal hydride reactivity.

A general MO scheme which interrelates the filled orbitals of a d^6 octahedral (ML_6 modelling $Mn(CO)_3L_2H$) and a d^8 trigonal bipyramidal complex (ML_5 standing for $Mn(NO)_2L_2H$) provides a more detailed insight into the electronic situation (Fig. 1).[47] Bookkeeping of the filled orbitals shows that two of the orbitals in octahedral symmetry (one of π and one of σ type) are transformed into the energetically high lying e' set in the D_{3h} symmetrical ML_5 molecule. From this picture it becomes immediately apparent that replacement of 3 CO ligands with 2 linear NO (NO^+)

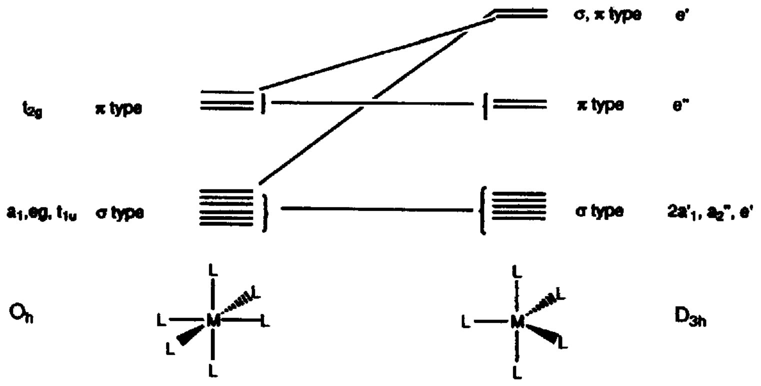


FIGURE 1

moieties in the d^6 complexes, with the nonbonding t_{2g} set filled, leads to a d^8 electron configuration with four (doubly) occupied metal oriented orbitals (e' and e'' set). The degenerate orbitals of e' symmetry are energetically quite high lying and hence add to the electron richness of the metal center. In a first approximation this picture can be applied to the description of the electronic situation in complexes of the type, $Mn(NO)_2L_2H$. One should keep in mind, however, that three MO's of the e' and e'' sets with π symmetry are considerably lowered in energy due to backbonding to the strong π acceptor NO. The remaining fourth orbital of the original e' set is mainly of σ-symmetry with respect to NO binding, hence almost unaffected and left at relatively high energy leading to a low first ionization potential in this type of compounds. It is noteworthy that Pearson[48] has already predicted reduced group electronegativities for nitrosyl substituted metal fragments based on MO electronegativities, in accord with the high energetic level of the HOMO. Compared with its octahedral $Mn(CO)_3L_2H$ congeners, an increased $M^{\delta+}-L^{\delta-}$ polarity of all metal ligand bonds including the M–H bond may therefore be expected for the isoelectronic dinitrosyl complexes. This electronic mechanism is not merely tied to NO disubstitution; moreover, it is expected to be operative in nitrosyl substituted complexes in general. The strength of this effect is, however, dependent on the degree of NO substitution (mono, di, tri).

Fenske–Hall calculations on $CpCr(NO)_2H$ carried out by Bursten *et al.* demonstrate that this complex also is in accord with the

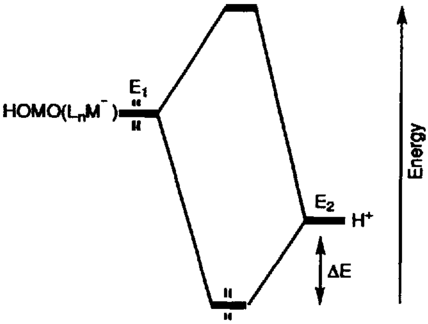
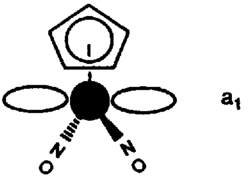


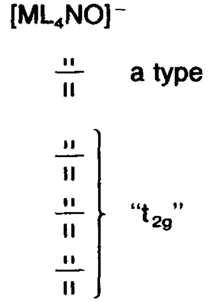
FIGURE 2

simplified electronic picture described above.[49] The electronic structure of $CpCr(NO)_2H$ has been found to be electronically very different from its $CpFe(CO)_2H$ and $CpCr(CO)_3H$ relatives.[50] The calculations revealed a relatively small HOMO-LUMO gap, which is accompanied by a substantial separation of the high lying HOMO from the second highest molecular orbital, the SHOMO. For a better understanding Bursten *et al.* suggested to view these $CpM(NO)_2H$ species as protonated $CpM(NO)_2^-$ anions. The protonation is expected to take place at the HOMO, thus leading to an energetically quite high lying M–H bonding orbital. The simplified orbital scheme for this two centered interaction demonstrates that the high lying HOMO causes a weakening of the covalent bonding and leads to an enhanced hydridic polarization of the M–H bond, as expressed by a small splitting energy ΔE, where ΔE is proportional to $S^2/|E_2 - E_1|$ according to MO perturbation theory (Fig. 2).[51] The substantial HOMO/SHOMO gap in these complexes is mainly a consequence of the predominantly nonbonding character of the energetically rather high lying a_1 orbital, the HOMO, which is shown below.



It is an interesting feature of these complexes that the energetic position of the HOMO is essentially determined just by the Coulomb energy of the metal d orbitals, since this would allow us to adjust the energetic level of the HOMO by the appropriate choice of the transition metal. This is best exemplified for the isoelectronic substitution series in which CO is replaced by NO and the metal center is substituted by its neighbour to the left in the periodic table. Due to the concomitant increase in the ionization potential of the transition metal, the HOMO will then be found at higher energy in the isoelectronic nitrosyl complex. The three energetically lower lying non-bonding (π-type) orbitals in $CpML_2$ compounds, normally denoted as the "t_{2g}" set,[52] show strong interaction with the π acceptor ligands and carry a great deal of their orbital character. Hence, they are found at low energy, especially in the case of L = NO. In this way the HOMO/SHOMO gap is increased in nitrosyl substituted cyclopentadienyl complexes.

C_s symmetrical $CpML_2$ fragments have the same type of frontier orbitals as square pyramidal ML_5 units. Therefore the interesting question arises, whether the NO ligand has an electronic influence, similar to that described above, in the anionic fragments, ML_5^-. A realistic case is given by the square pyramidal $ML_4(NO)^-$ species (M = Cr, Mo, W) with the NO ligand in apical position. These complexes have a d^8 electron configuration with a "one above three" frontier orbital structure.[47]



In a first approximation, only the three orbitals at lower energy, the former "t_{2g}" set in octahedral symmetry, will participate in backbonding to the NO π acceptor. Since these orbitals are of π symmetry, they would, however, not be involved in the interaction with the empty 1s acceptor orbital of a proton. Note that this is the orbital representative of the protonation reaction of the ML_4NO^- fragment which would yield the neutral trans nitrosyl hydride complex.

As in the case of $CpCr(NO)_2^-$, the energetically high lying a type orbital, the HOMO, is again of σ-symmetry and hence not perturbed by π acceptor interactions. Also, the energy of this orbital is strongly determined by the Coulomb energies of the transition metal orbitals. Hence, as another example of the isoelectronic substitution series, the a type HOMO in the 18 electron compounds $[WL_4NO]^-$ and $[ReL_4CO]^-$ would be expected at higher energy for the tungsten complex due to the lower ionization potential of the W atomic orbitals. Based on the arguments described for $CpCr(NO)_2^-$, an enhanced hydridic character of the M–H bond may also be put forward for the corresponding hydride complexes, $ML_4(NO)H$, since it is once again the very high lying a type HOMO which is mainly involved in bonding to the hydrogen ligand.

From this orbital analysis we can expect a weakening of covalent L_nM–H bonding with concomitant polarization of this bond toward more hydridic character in the transition metal nitrosyl complexes. Although this refers only to the covalent part of the transition metal hydrogen bond, the latter energy term might dominate M–H bond dissociation energies, and therefore also lead to weak M–H bonds in hydridically polarized M–H compounds. Since there are no conclusive experimental M–H bond dissociation enthalpies (BDE's) for transition metal nitrosyl hydride complexes available so far, the latter conclusion must still remain somehow speculative. It should be noted, however, that based on Pauling's equation for the determination of BDE's, Bercaw and Labinger[53] have proposed that electropositive transition metals form only weak metal hydrogen bonds, which would cope with our theoretical derivation for nitrosyl hydride complexes.

With respect to hydride transfer to organic substrates, the considerable HOMO/SHOMO gap in the hypothetical anions is also of great importance. Since the corresponding monocationic complexes formed in these reactions are therefore of considerable stability, the product side of these reactions would be expected to be particularly favoured. This thermodynamic preference together with the enhanced hydricity and the concomitant presumed low kinetic barriers in these complexes prompted us to initiate a research program aimed at exploring the predicted highly reactive character of the M–H bond in these compounds.

PHYSICAL PROPERTIES OF NITROSYL HYDRIDE COMPOUNDS

At first glance M–H bond distances would be expected to contain the most interesting structural information with respect to structure reactivity correlations. Unfortunately, however, values obtained from X-ray crystallography are not very reliable; quite accurate metal hydrogen bond distances can be determined, on the other

TABLE II

M–H distances from temperature dependent NMR relaxation time measurements ($T_{1\mathrm{min}}$) of selected nitrosyl and non-nitrosyl containing manganese and rhenium complexes (Ref. 54).

Compound	$r_{\mathrm{M-H}}$[Å]
$\mathrm{Mn(NO)_2(PEt_3)_2H}$	1.59 ± 0.02
$\mathrm{Mn(CO)_3(PEt_3)_2H}$	1.62 ± 0.02
$\mathrm{Re(CO)_3[P(OiPr)_3]_2H}$	1.71 ± 0.05
$\mathrm{Re(CO)_2(PMe_3)_3H}$	1.73 ± 0.03
cis-$\mathrm{Re(CO)(PMe_3)_4H}$	1.69 ± 0.03
$\mathrm{Re(CO)(NO)(PMe_3)_2H_2}$	1.72 ± 0.04, 1.75 ± 0.05*
$\mathrm{Re(CO)(NO)(PCy_3)_2H_2}$	1.71 ± 0.08, 1.74 ± 0.04*
$\mathrm{Re(CO)(NO)[P(OiPr)_3]_2H_2}$	1.72 ± 0.05, 1.70 ± 0.08*

*H trans to CO.

hand, in neutron diffraction studies. Due to the necessity of an appropriate neutron source and the requirement of sizable single crystals, however, this method is somewhat limited for routine measurements. Hence, it is not surprising that just two neutron single crystal investigations have been carried out for this class of compounds, e.g., for the hydride bridged bimetallic complexes $\mathrm{W_2(CO)_9(NO)H}$ [39] and $\mathrm{W_2(CO)_8(NO)(P(OMe)_3)H}$.[40] In search of a facile routine method, our group has therefore turned toward temperature dependent NMR $T_{1\mathrm{min}}$ relaxation measurements which proved to be a reliable and practical tool for the determination of M–H bond distances in solution (Table II).[54]

Table II demonstrates that M–H bond distances are basically invariant to the substitution pattern at the metal centers. This becomes immediately apparent, if one compares the analogous complexes with CO, NO or phosphorus ligands. While the observed differences in bond lengths are mostly within experimental error, a trend is, however, noticeable: Longer bond distances are, in general, observed for the heavier 5d transition metals as might have been expected solely based on the covalent radii of the metal centers. Regardless of the limited amount of available data, M–H bond distances seem not to be appropriate to allow structure reactivity correlations.

Hence, we set out to search for other relevant spectroscopic properties which might show correlation with general electronic features. Our NMR studies on $\mathrm{W(NO)(CO)_2L_2H}$ complexes[11] with varying phosphorus ligands, L, revealed, however, no correlation of chemical shifts or coupling constants of the ^{1}H, ^{13}C, ^{31}P, ^{183}W nuclei with Tolman's electronic parameters of these ligands. Nevertheless, we observed that NO substitution causes a marked low field chemical shift of the resonances for the metal bound hydrogen atoms trans to the NO ligand (cf. Table I). This is best demonstrated for the $Re(CO)(NO)L_2H_2$ series,[22a] in which the ^{1}H NMR resonances of the hydrogen ligand trans to NO are over 3 ppm downfield from the chemical shift of the other hydride ligand located trans to CO.

In a further attempt to elucidate some details of the electronic structure in these transition metal nitrosyl hydride compounds, we investigated the IR vibrations of the NO, CO and hydride ligands for a series of $M(CO)_2(NO)L_2H$ complexes ($M = Cr, W$), where $L =$ phosphorus donor.[7,11] Concomitant with the observation of low wavenumbers for the $\nu(NO)$ and $\nu(MH)$ bands, we found a linear correlation of Tolman's electronic parameters for the phosphorus ligands with both types of vibration, i.e., the more electronically donating ligands lead to vibrations of lower energy. With regard to the M–H vibration this relationship presumably reflects weakening of the covalent M–H bonding upon charge increase on the metal center, i.e., induced by the stronger phosphorus donors, the LUMO of the corresponding L_nM^- anion is shifted to higher energy and hence leads to a smaller splitting energy. Note that low $\nu(MH)$ stretching frequencies supposedly indicate transition metal hydride compounds with enhanced activation of the hydride ligands. Assuming also parallel electronic dependencies of the $\nu(NO)$ and $\nu(MH)$ bands on other nitrosyl hydride complexes, we propose that the better accessible $\nu(NO)$ stretching frequencies can be used to judge the degree of M–H activation. As a rule of thumb, the NO stretching frequencies should be found below 1680 cm^{-1} for reactive systems with enhanced hydricity.

HYDRIDIC REACTIVITY OF NITROSYL HYDRIDE COMPLEXES

Based on the electronegativities of the transition metals and H, it is generally assumed that most transition metal hydrogen bonds are covalent with a polarization toward a hydridic H.[55–57] Since quite a number of transition metal hydride complexes react in solution in fact as acids,[55] it should become immediately apparent that it is not legitimate to transfer this knowledge derived for isolated molecules in the gas phase unreservedly to solution phase chemistry.

In order to explain protonic/hydridic preferences of transition metal hydrides, Pearson[48] has defined the equilibrium shown below:

$$L_nM^-(g, solv) + H^+(g, solv) \rightleftharpoons L_nM^+(g, solv) + H^-(g, solv)\ \Delta H_{ph}$$

In the gas phase the equilibrium position is only dependent on the Mulliken electronegativities of L_nM and H ($\Delta H_{ph} = \Delta H(redox)$).[58] From $H_{ph} = \Delta H(redox) + \Delta H(solv)$, it can be seen that the equilibrium in solution is expected to be strongly influenced by solvent effects ($\Delta H(solv)$ = enthalpy of solvation). Since $\Delta H(solv)$ for H^+ in water ($\Delta H_{hydr}(H^+) = 267$ kcal/mol) is exceedingly higher than the heat of hydration for H^- ($\Delta H_{hydr}(H^-) = 108$ kcal/mol; $\Delta H_{hydr}(L_nM^-) \approx \Delta H_{hydr}(L_nM^+)$), the overall heat of solvation for this process is strongly positive.

For most metal systems the latter energy term is dominant and ΔH_{ph} is therefore also positive. Hence, hydridic reactivity of transition metal hydrides can only be achieved in solution, if the metal fragments possess low orbital electronegativities, i.e., are easily oxidized ($E^o(L_nM^-) << 0$). As derived from the quantum theoretical description of the transition metal nitrosyl hydride complexes, the nitrosyl ligand gives rise to energetically high lying HOMO's, thus leading to readily oxidizeable compounds. A shift to the right side of the equilibrium, i.e., toward more hydridic behaviour, may hence be put forward for this type of complex.

Recently, we have determined ionicities of transition metal hydrogen bonds in nitrosyl substituted and other transition metal hydride complexes from temperature dependent T_{1min} deuterium NMR relaxation time measurements.[59] Albeit somehow expected, the results were still quite surprising, in that the nitrosyl deuteride complexes exhibited a highly ionic L_nM-D bond character which is in the range of early transition metal hydride complexes.[60] This is best exemplified for the two complexes, $W(CO)_2(NO)(PMe_3)_2D$ and $Mn(NO)_2(PEt_3)_2D$, which possess 76 and 75%, respectively, hydridic character in their M–D bonds and hence compare favourably to the ionic contribution of 79% determined for the Zr–D bond in Cp_2ZrD_2.

We and others have also demonstrated the hydridic nature of the L_nM–H bond in the $W(CO)_2(NO)L_2H$,[12,61] $Re(CO)(NO)L_2H_2$,[22a,63] $Mn(NO)_2L_2H$ [16] and $CpW(NO)_2H$ [8] complexes by their reactions with weak or moderately strong acids. Protonation of the hydridic hydrogen ligand with concomitant evolution of H_2 takes place at ambient temperature or below (Eq. (1)):

$$L_nM{-}H + HB \rightarrow L_nM{-}B + H_2,$$

$$L_nM = W(CO)_2(NO)L_2,\ Re(CO)_2(NO)L_2H,\ Mn(NO)_2L_2,$$

$$L = \text{phosphine, phosphite;} \qquad (1)$$

$$HB = PhOH,\ MeCOOH,\ CF_3COOH,$$

$$L_nM = W(NO)_2Cp;\ HB = p\text{-}MeC_6H_4SO_3H.$$

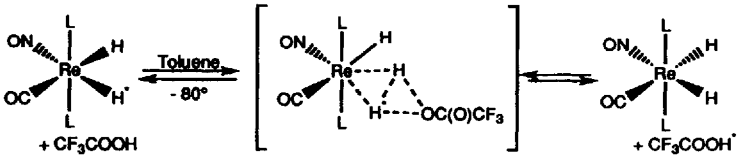
As a further probe for the basic character of the M–H bond in nitrosyl hydride complexes, we examined the reactivity of the hydride ligand toward Lewis acids such as $BH_3 \cdot THF$, BF_3, $B(C_6F_5)_3$ and Ph_3C^+ with a series of $W(CO)_2(NO)L_2H$ derivatives.[27] Quite unstable $W(CO)(NO)L_2(\eta^2\text{-}BH_4)$ complexes were obtained in the reactions with $BH_3 \cdot THF$; the η^2 binding mode of the BH_4^- ligand of the reaction products could be confirmed unambiguously by an X-ray crystal structure for the compound with L = PMe_3.[61b]

In donor solvents, S, complete abstraction of the hydride ligand was observed with the other Lewis acids BF_3, $B(C_6F_5)_3$, and $Ph_3C^+BF_4^-$, yielding the solvent coordinated complexes, $[W(CO)_2(NO)L_2(S)]^+$ (see also Ref. 12). The analogous reaction of $CpW(NO)_2H$ with $Ph_3C^+BF_4^-$ in acetonitrile leads to the corresponding cationic compound $CpW(NO)_2(CH_3CN)^+BF_4^-$ [8]; the related reaction of ReCp(CO)(NO)H with the tropylium cation, $C_7H_7^-$, affords upon hydride abstraction $ReCp(CO)(NO)(\eta^2\text{-}cycloheptatriene)^+$.[62] It is noteworthy that the hydride bridged cationic dimer, $[Cp(NO)_2W(\mu\text{-}H)W(NO)_2Cp]^+$, is obtained instead, if the latter reaction is carried out in the absence of donor solvents. In a similar manner the bimetallic complex, $Cp(NO)_2W(\mu\text{-}H)Cr(CO)_5$, which contains a weak Cr–W bond, can be built up.[38]

Concerning the reactivity of the M–H bond in nitrosyl hydride complexes, we were also interested to see whether we could observe a specific trans influence of the NO ligand. In order to address this point, we investigated the protonation reaction of the pseudooctahedral dihydride compounds, $Re(CO)(NO)L_2H_2$ (L = phosphorus donor).[63] Since these complexes contain two diastereotopic metal hydride ligands, one trans to a NO and the other trans to a CO ligand, they could in principle exhibit different reactivity in their reaction with acids.

Protonation with excess CF_3COOH under polar conditions leads to formation of the non-classical dihydrogen complexes, $[Re(H)(\eta^2\text{-}H_2)(CO)(NO)L_2]^+$. So far, we have, however, not been able to determine the actual structure of the latter compounds in solution from the NMR data. The protonation reactions have been shown to be relatively slow and were also found to be thermodynamically quite unfavourable.

If the CF_3COOH acid is, however, added in approximately stoichiometric amount and in an unpolar solvent, quite fast *regioselective* H/H exchange of the hydride ligand trans to the nitrosyl group is observed. This has been shown to occur with the assistance of the acid anion[63] (Eq. (2)):



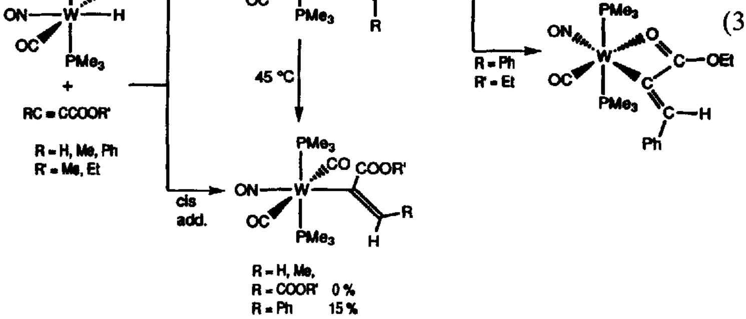
L = PMe$_3$, P(OiPr)$_3$ (2)

The high regioselectivity of this process has been attributed to the strong π acceptor property of the NO ligand, which is operating most efficiently in the trans position. The formation of non-classical dihydrogen ligands trans to the NO ligand is also presumed to be less favourable, due to the strong charge flow of the dihydrogen (H_2) moiety to the NO group. It should be noted that the destabilizing influence of the NO ligand in non-classical H_2 complexes appears to be general and was observed first in hydrogenation studies of $Co(NO)(CO)_3$.[64] Hence, we assume that binding of the counterion to the ReH_2 moiety is required to stabilize the transition state, thus lowering the activation barrier for this process.

INSERTION REACTIONS OF NITROSYL HYDRIDE COMPLEXES

The most prominent reaction types of transition metal nitrosyl hydride complexes with respect to the M–H moiety are (a) the M–H alkyne insertion reaction and (b) the intermolecular hydride transfer to carbonyl containing organic substrates (mainly aldehydes). From the electronic structure of this class of compounds derived in the theoretical section, an enhanced reactivity toward these substrates was already predicted. In this section we will try to support this perspective with results obtained from reactivity studies.

(a) Alkyne Insertion: Facile insertion reactions have been reported for nitrosyl hydride compounds of $W(CO)_2(NO)L_2H$,[61a,65a] $Mn(NO)_2L_2H$ (L = phosphorus donor),[16] $CpRe(CO)(NO)H$ [65b] and for $Ru(NO)(PPh_3)_3H$.[33b] For the $W(CO)_2(NO)(PMe_3)_2H$ complex of this series, regioselective insertion of the methyl propiolate derivatives, $RC\equiv CCOOMe$, where R = H, Me, Ph, COOMe, was observed. Much to our surprise, however, these reactions occurred apparently via trans rather than cis addition of the M–H bond to the alkyne (Eq. (3)):



(3)

Formation of the trans insertion product has been confirmed for HC≡C-COOMe in deuterium labelling experiments using either the alkyne or tungsten isotopomer.[65a] It should be noted that alkyne insertion reactions with the Schwartz reagent, $Cp_2Zr(H)(Cl)$,[66] proceed exclusively through cis addition. The latter stereochemistry has been explained with an intramolecular hydride migratory insertion mechanism, i.e., the alkyne ligand is presumed to be precoordinated to the Lewis acidic (16 e^-) Zr center. Although either bending of the NO ligand or ligand extrusion might be considered to give a 16 electron configurated reactive transient from 18 e^- nitrosyl hydride complexes, this scenario is hard to reconcile, since it would quite certainly lead to higher activation barriers for the insertion process. Also, this mechanism would require further rearrangement of the primary cis addition products to the observed trans addition products. Nevertheless, some evidence for such a pathway is provided since the cis addition product was obtained to a small extent (15%) with the more sterically demanding derivative, PhC≡CCOOMe. The predominantly formed complex, however, is the expected E configurated complex (85%). This is apparently the kinetically controlled product and can be isomerized to the thermodynamically more stable Z configurated derivative at temperatures higher than those required for the insertion reaction. Steric relief in this compound is also accomplished through substitution of a cis CO ligand by the oxygen donor of the ester group giving the metallacycle shown in Eq. (3).

A tungstenacyclic complex is also obtained as final product with acetylene dimethylcarboxylate as substrate. In the course of this facile reaction the short-lived trans addition product ($\tau_{1/2} \approx 10$ min at RT) is initially formed and then also substitutes a cis CO ligand to give the five-membered metallacycle (Eq. (3)).

It deserves a special mention that in sharp contrast to the stereoselectivity observed for the hydridic transition metal complexes, the opposite stereochemistry, i.e., β metallation, was found for the alkyne insertion into *acidic* M–H bonds.[67a–g] Even though the reactions might proceed in these cases via a different mechanism, this result suggests that the extent of hydricity in the M–H bond determines at some stage of the reaction the regioselectivity of the insertion process.

An even more complicated alkyne insertion mechanism with a

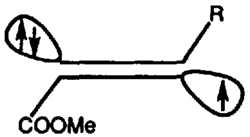


FIGURE 3

rate determining one electron transfer step has been proposed by Clark and co-workers[67h] for the alkyne insertion reactions of a trans PtL_2H_2 complex. Once again, these reactions also proceed with α metallation regioselectivity. It has been suggested that the charge transfer process generates the radical cage pair of $PtL_2H_2^{\overset{+}{\cdot}}$ and the alkyne radical anion; the preferred structure of the latter is shown in Fig. 3. Since no cage escape products could be detected, consecutive product formation steps of these transients have to be assumed to occur faster than diffusional escape from the cage. Concerning the stereochemical course of this mechanism, two different issues, e.g., the observed regio- and stereoselectivity, have to be addressed. Both are essentially related to the structural preferences of the alkyne radical anion and also, though to a smaller extent, to the electronic situation in the cationic metal radical fragment. Although one has to be aware of a Curtin–Hammet type scenario, in which actually only the species present in lower equilibrium concentration is involved in the reaction, it is presumed that the (experimentally confirmed) thermodynamic preference for the E configurated alkyne radical anions dictates the anti addition selectivity of the insertion reaction. Note that this would not demand any participation of the metal fragment in the selective step. The observed regioselectivity, on the other hand, however, is presumably partly due to the preference of the L_nMH^+ radical cation to undergo either hereto- or homolytic M–H bond cleavage.

$$L_nMH + HC\equiv CR \rightarrow [L_nMH^{\overset{+}{\cdot}}, HC\equiv CR^{\overset{-}{\cdot}}],$$

$$H^+ + L_nM\cdot \leftarrow L_nMH^{\overset{+}{\cdot}} \rightarrow L_nM^+ + H^\cdot.$$

This is rationalized by the fact that the alkyne radical anion is ambident, i.e., it can act as base and abstract the H ligand as proton from $L_nMH^{\overset{+}{\cdot}}$ and also as radical ($H^\cdot$ abstraction), the latter leaving a L_nM^+ fragment behind. Although it is certainly difficult to predict relative rates for both obviously fast reaction steps, a preference for the H$^{\cdot}$ radical abstraction pathway is deemed for the more hydridically polarized compounds. Formation of the observed products would then occur through collapse of the L_nM^+ fragment and the vinyl anion (formed from the alkyne radical anion by H abstraction). The regioselectivity of this process would once again be determined by the relative stabilities of the alkyne radical anions. Although experimental data for the relative stabilities of the two possible different regioisomers of the propiolate radical anion are not available, it seems reasonable to assume a greater stability for the anionic site in the α position to the ester function (as shown above). Note that based on this structural preference the observed regioselectivity would be predicted.

Clearly, further mechanistic investigations are required to establish the mechanism(s) of the alkyne insertion reaction. Simply judging from the strict regioselectivity, however, a transition state with *antara* orientation of the alkyne and the M–H bond is implied for the trans addition products. Note that this would be also in accordance with the ground state bond polarizations of the reactants (Fig. 4).

Before we inspect the reactivity of the nitrosyl hydride complexes toward carbonyl containing compounds, we will briefly address the chemoselectivity of these complexes for substrates which contain both C–C and C–O multiple bonds. In the reaction of $W(CO)_2(NO)[P(OiPr)_3]_2H$ with propiolic aldehyde, exclusive formation of the C–C insertion product was observed.[68] The same chemo-preference has been reported by Hillhouse *et al.*[69] for the reaction of carbon suboxide (C_3O_2) with $W(CO)_2(NO)(PPh_3)_2H$, which leads to a formyl ketenyl ligand unit. From these observations we may conclude that the chemoselectivity of these compounds is apparently not dominated by the affinity of the tungsten metal center toward oxygen. In addition, these complexes do not

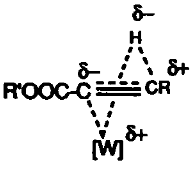
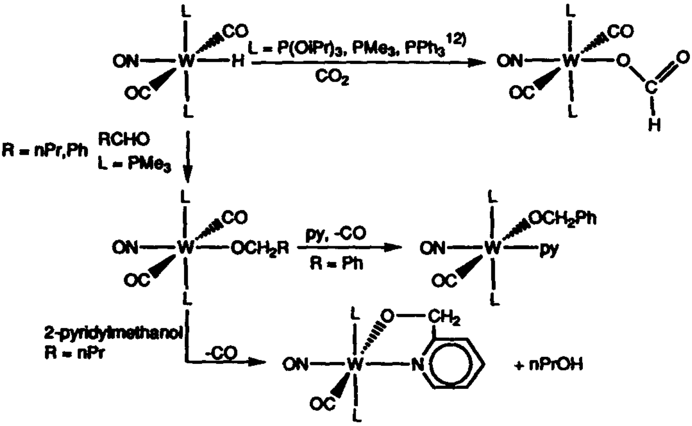


FIGURE 4

exhibit such a pronounced oxophilicity as early transition metal hydride compounds. It is noteworthy at this point that reduced oxygen affinity of the metal center is considered one of the prerequisites for the catalytic hydrogenation of carbonyl containing substrates.

(b) Intramolecular Hydride Transfer Reactions: In the previous sections we have stressed the activated character of the M–H bond in nitrosyl hydride complexes toward intramolecular hydride transfer reactions. Support for the enhanced hydricity in these compounds is indeed provided by the observed difference in reactivities for the two relatives of the isoelectronic substitution series, mer,trans $Re(CO)_3(PMe_3)_2H$ and trans $W(CO)_2(NO)L_2H$ ($L = P(OiPr)_3$, PPh_3, PMe_3), toward CO_2 and the more polar aldehydes. While *no* reactions were observed for the Re complex,[16] the isoelectronic nitrosyl tungsten analogues undergo facile hydride transfer to these substrates at ambient temperature.[12,68,70–72]



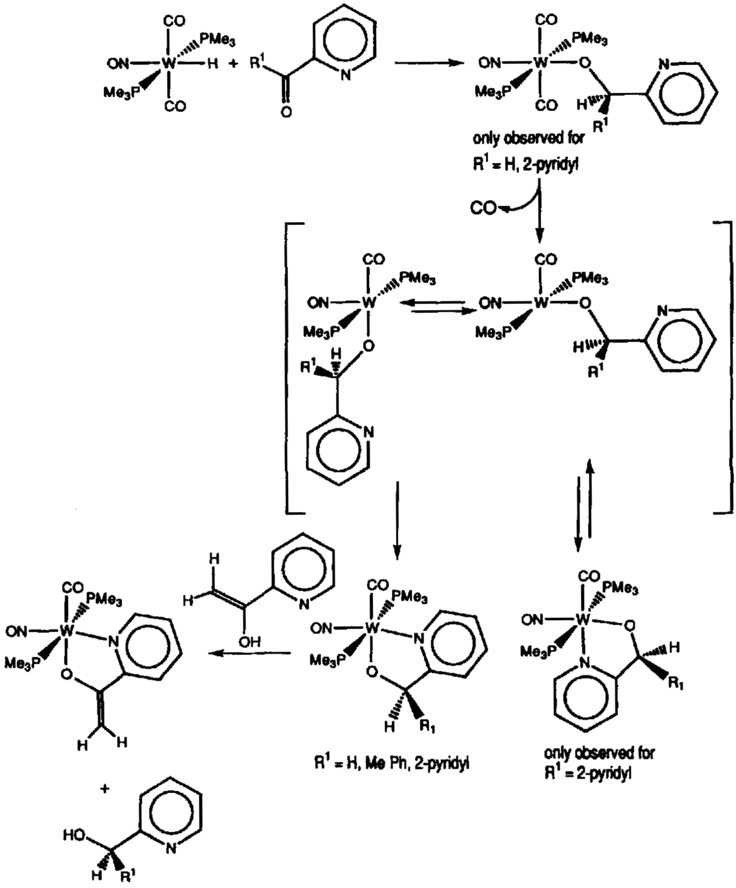
(4)

As depicted in Eq. (4) stable η^1-formate complexes have been obtained with a number of phosphorus donor substituted tungsten analogues.[12,68,72] Hillhouse and co-workers have in addition reported W–H bond insertion of various unsaturated substrates for $W(CO)_2(NO)(PPh_3)_2H$, e.g., diazonium salts yielded diazene complexes, CS_2 a thioformate and carbodiimide a formadimato compound.[12]

In the reactions of $W(CO)_2(NO)(PMe_3)_2H$ with alkyl and aryl aldehydes, the quite unstable, non-isolable alk- and aryloxy derivatives were obtained.[70,71] Due to the cis labilizing effect of the alkoxide unit, these reaction products suffer from facile CO loss and hence decompose rapidly. However, if pyridine is added to the reaction mixture of the aldehydes and the hydride complexes, the reaction times are unaffected and the primary products can be stabilized as the pyridine adducts.[71] Note that a concomitant rearrangement to the isomer with the NO group trans to the pyridine ligand is observed. Alternatively, we succeeded in converting the unstable primary alkoxide reaction products by alkoxide exchange with 2-pyridyl methanol.[70] This is best exemplified for the reaction product with propanal, $W(OPr)(CO)_2(NO)(PMe_3)_2$, which yields CO, propanol and the 2-pyridylmethoxide complex with the coordinatively robust chelating unit (Eq. (4)).

In order to study these hydride transfer reactions in greater detail, modified aldehydes with additional donor groups, which might stabilize the insertion products through the formation of a chelate ring, were sought. The reactions of $W(CO)_2(NO)(PMe_3)_2H$ with a series of substituted pyridylcarbaldehydes and pyridyl ketones are summarized in Scheme 1.[70] Although the intermediacy of the η^1 bonded tungsten alkoxy compound was only confirmed for the aldehydes with R^1=H pyridin-2-yl, R^2=H, we assume that these intermediates are also formed with the other substrates. Subsequent loss of CO, isomerization and coordination of the pyridine N-donor to the tungsten center then lead to the observed O,N-chelated complexes with the apparently thermodynamically preferred trans NO/N-pyridyl arrangement. It deserves mentioning that the reaction with the ketone substrate, methyl pyrid-2-yl ketone, is quite slow (several days at 50°C) and complicated by the fact that the initial insertion product is partly converted to the tungsten enolate complex and 1-(pyridin-2-yl) ethanol in the presence of excess methyl pyridin-2-yl ketone.

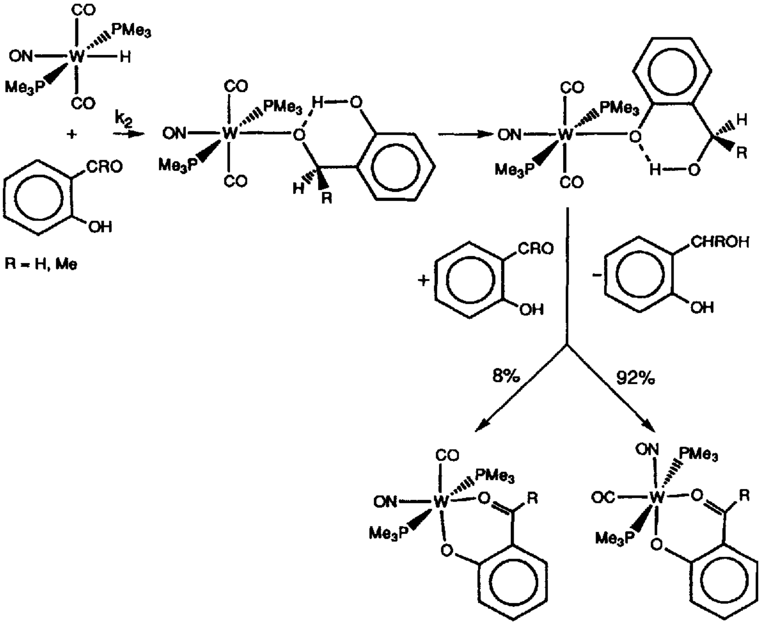
Since the hydride transfer to some aldehydes and, particularly to ketones, turned out to be quite a slow process (vide supra), we were pleased to note that significant acceleration of these reactions was observed in the presence of weak or moderately strong acids,



SCHEME 1

such as phenol or acetic acid.[61a,71] As a further probe for the H^+ promoted insertion, reactions of $W(CO)_2(NO)(PMe_3)_2H$ with salicylaldehyde were sought.[71] This aldehyde was deemed particularly interesting since it contains both the carbonyl and the acidic functionality in the same molecule, and also due to its chelating ligand potential which might stabilize some of the crucial intermediates or products along the reaction path. The salicylaldehyde reacts smoothly with $W(CO)_2(NO)(PMe_3)_2H$; in comparison with benzaldehyde, however, the hydride transfer to the salicylaldehyde is exceedingly faster. The reaction follows second order kinetics (k_2 = 0.06 $l \cdot mol^{-1} \cdot s^{-1}$) and is first order in the tungsten complex, as well as in the aldehyde.

Initially, the expected hydride transfer product, the benzyloxy complex, was formed, and could be characterized spectroscopically. Due to a fast rearrangement to the corresponding phenoxy compound, however, we were not able to isolate this intermediate. Also, on a related issue, the phenoxy complex appeared to be thermally unstable. We observed, however, that reaction of this compound with excess salicyladehyde (>2 equiv) leads in excellent yields to 2-dihydroxytoluene and the stable α formyl phenoxo isomers (depicted in Scheme 2). In this way an ionic hydrogenation of salicylaldehyde through formal addition of H^-, from the nitrosyl hydride complex, and H^+, from the phenol group, is achieved. It deserves mentioning at this point that similar reductions of carbonyl derivatives have been accomplished with $[W(CO_5H]^-$ as hydride donator in the presence of an acid.[73]

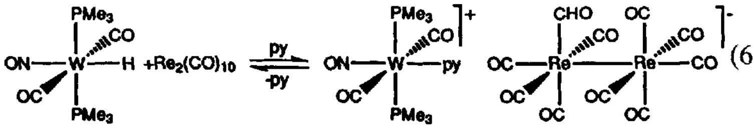


SCHEME 2

In further experiments we have found that the ionic hydrogenation can also be applied to o-acetyl phenol derivatives[71] (ketone relatives of salicylaldehyde) and β diketone substrates[74] (Eq. (5)). The carbonyl groups in these compounds appear mutually activated and are readily attacked by the $W(CO)_2(NO)(PMe_3)_2H$ reagent. As might have been expected based on the quite similar pK_a range of β diketones and phenols, the acidity of β diketones is sufficient, so that they can act as a proton source in these processes.

$$W(CO)_2(NO)(PMe_3)_2H + 2R(CO)CH_2(CO)R \xrightarrow{-CO} W(CO)(NO)(PMe_3)_2(\eta^2\text{-}[R(CO)CH(COR)]) + R(CHOH)CH_2(COR), \quad R = CF_3, CH_3, Ph \qquad (5)$$

These results raise interesting mechanistic questions about the hydride transfer step in the presence or absence of protons. Since precoordination of the aldehyde or ketone to the metal center is deemed quite unlikely in the absence of vacant coordination sites, we have proposed earlier that these reactions might proceed in analogy to CO_2 insertions through direct hydride transfer to the carbonyl group. As described for the alkyne insertion, an electron transfer mechanism with the intermediacy of radical species is again a reasonable alternative and has obtained some evidence from the pyridyl carbaldehyde insertion chemistry. Nevertheless, some support for the direct hydride transfer mechanism is provided by the reaction of $W(CO)_2(NO)(PMe_3)_2H$ with $Re_2(CO)_{10}$ in the presence of pyridine (Eq. (6)), since no CO ligand substitution products of the Re_2 fragment, indicative of a electron transfer promoted 17 e^- $Re(CO)_5\cdot$ radical intermediate, could be detected.[75]



(6)

The formation of the well known $[Re_2(CO)_9CHO]^-$ species can be monitored by IR and ^1H NMR spectroscopy.[76] It is noteworthy that hydride transfer to metal carbonyl ligands has otherwise been restricted to main group hydrides and early transition metal hydrides such as $Cp_2^*ZrH_2$.[77] It is clear, however, that this is no proof for a direct hydride transfer mechanism, and detailed mechanistic investigations are required to distinguish these alternatives.

The role of the proton source in the acid promoted reaction is also unclear so far. In principle, there are two possible sites, e.g., the L_nM-H and the $>C=O$ moiety which might interact with the proton and hence accelerate the hydride transfer. As described earlier, nitrosyl hydrides undergo facile H/D exchange with weakly acidic compounds, such as methanol-d_1 (CH_3OD).[11] This scrambling process may also be of some relevance for the reduction of aldehydes and might involve a cyclic or linear L_nMH/HA arrangement which can deliver the appropriate geometry for a near "simultaneous" transfer of H^- and H^+ to the organic substrates (Fig. 5). Alternatively, the acid promoted reaction may proceed via protonation of the carbonyl group. This is, however, hard to reconcile, since kinetically relevant concentrations of the very acidic protonated intermediates, $>C-O-H^+$, would not be expected with the quite weak acid phenol (Fig. 6).

Up to this point most of the reactivity studies were reviewed for the $W(CO)_2(NO)L_2H$ complexes. In order to demonstrate that the high reactivity is not due this specific metal/ligand combination but instead related to the genuine "nitrosyl effect," we will briefly

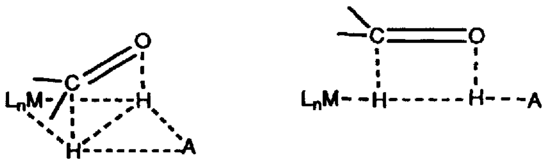


FIGURE 5

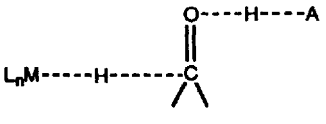


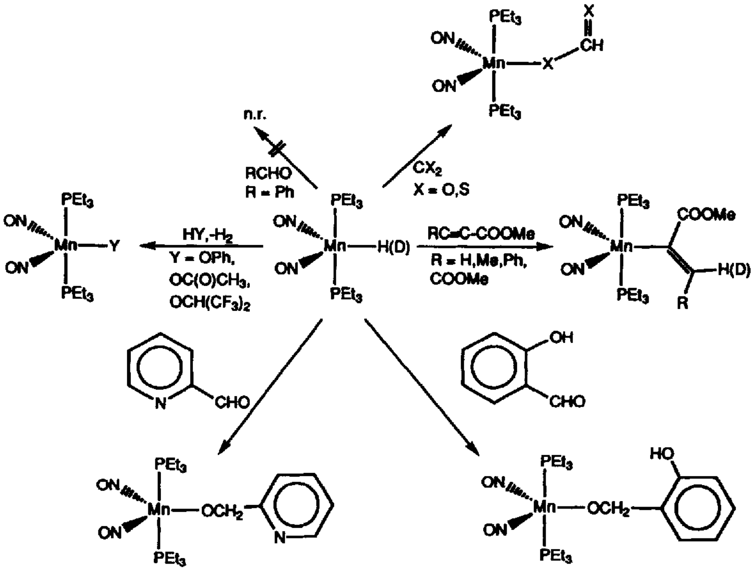
FIGURE 6

examine the intensively investigated chemistry of $Mn(NO)_2L_2H$ complexes.[16]

As can be seen from Scheme 3, the reaction chemistry of $Mn(NO)_2(PEt_3)_2H$ does closely resemble that of the $W(CO)_2(NO)_2L_2H$ complexes. It is worth mentioning that except for some acetylene insertions none of the reactions shown in Scheme 3 can be accomplished with the isoelectronic compound, $Mn(CO)_3(PEt_3)_2H$, which adds further evidence to the nitrosyl effect.

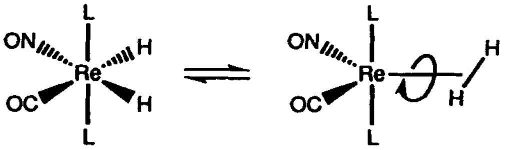
DYNAMIC BEHAVIOUR OF NITROSYL HYDRIDE COMPLEXES

It has been mentioned earlier that non-classical (H_2) complexes are apparently destabilized by NO in the ligand sphere of transition metal complexes. Despite this overall NO destabilizing effect, quantum theoretical calculations imply that the formation of dihydrogen intermediates from classic dihydride complexes is facili-



SCHEME 3

tated through NO substitution.[78] This is rationalized by an overall stronger destabilizing influence of the NO ligand for the dihydride complex with respect to the η^2 dihydrogen species. Preliminary evidence for this phenomenon could be provided through the $Re(CO)(NO)L_2H_2$ compounds (L = $P(OiPr)_3$, PMe_3, $P(iPr)_3$, PCy_3) which show dynamic behaviour between 40–100°C. The proposed reaction pathway for the intramolecular H/H exchange of the diastereotopic hydride ligands invokes the intermediacy of non-classical H_2 complexes[79] (Eq. (7)).



L = $P(OiPr)_3$, PMe_3, $PiPr_3$, PCy_3 (7)

Support for this mechanism was provided by a detailed MO analysis, which demonstrates that NO substitution promotes all crucial orbital conversions of this process. In addition, the calculations implied that the hypothetical dinitrosyl dihydride complexes of the type, $Re(NO)_2L_2H_2^+$, might even preferably exist in the non-classical form. Fluxional behaviour has also been reported for the isoelectronic $Os(CO)(NO)L_2H_2]^+$ compounds,[80] but their rearrangement mechanism has so far not been investigated.

CONCLUDING REMARKS

This account was meant to address by way of selected examples one of the major issues of stoichiometric and catalytic organometallic transformations which is probably summarized best in the following question: "How can we tune a prominent metal ligand bond toward enhanced reactivity and selectivity?" In this regard we have focussed in this review on nitrosyl substitution as a chemical tool to make metal hydrides more reactive toward alkyne insertion and carbonyl reduction chemistry. The hydridic polarization of the metal hydrogen bond in nitrosyl hydride complexes was deduced from MO theory and experimentally confirmed by physicochemical measurements and in reactivity studies.

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