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Reactivity of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (tim^{Me} = 2-Mercapto-1-methylimidazolyl) toward Neutral Substrates

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The complex [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**) (tim^{Me} = 2-mercapto-1-methylimidazolyl) reacts with a variety of neutral substrates to afford new complexes featuring the dihydrobis(2-mercapto-1-methylimidazolyl)borate coordinated in a bidentate or unidentate fashion. By treating **2a** with unidentate ligands, the mononuclear complexes [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(L)] (L = imidazole (**5**), 4-(dimethylamino)pyridine (**6**), *tert*-butylisonitrile (**7**), triphenylphosphine (**8**)) were formed, upon replacement of the agostic B–H···Re bond by the correspondent unidentate ligand. With potentially bidentate substrates, **2a** is transformed into mononuclear or dinuclear complexes, depending on the atom donor set of the reacting substrates. Reaction of compound **2a** with ethylenediamine (en) gave the complex [Re{κ^1-H$_2$B(tim^{Me})$_2$}(CO)$_3$(en)] (**9**), because of cleavage of the agostic interaction, dechelation of one mercaptoimidazolyl ring, and bidentate coordination of the amine. By contrast, 1,2-bis(diphenyl)phosphinoethane (dppe) is not able to replace the mercaptoimidazolyl ring, and the dimer [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$]$_2$(μ-dppe) (**10**) was formed. The novel Re(I) tricarbonyl complexes (**5**–**10**) have been fully characterized, including by X-ray diffraction analysis in the case of **6**, **8**, **9**, and **10**. The X-ray diffraction study confirmed the unprecedented unidentate coordination mode of the dihydrobis(2-mercapto-1-methylimidazolyl)borate in complex **9**.

Introduction

Poly(mercaptoimidazolyl)borates, which can be seen as soft analogues of poly(pyrazolyl)borates, have been recently introduced,[1−13] and their use is expected to extend the scope of the rich chemistry developed with poly(pyrazolyl)-borates.[14]

Our research group has been involved in the chemistry of rhenium complexes stabilized with poly(pyrazolyl)borates,[15] and recently, we have extended our research work to poly-(mercaptoimidazolyl)borates.[16] Different organometallic complexes of the type [M{κ^3-HB(tim^{Me})$_3$}(CO)$_3$] (**1**) and [M{κ^3-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (R = H (**2**), Me (**3**), Ph (**4**)) (M = Re, $^{99/99m}$Tc) have been synthesized and characterized.[16] Relative to poly(pyrazolyl)borates, the interesting feature of the poly(mercaptoimidazolyl)borates, for biomedical applications, is their high stability in water and the possibility

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(1) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.
(2) Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680.
(3) Santini, C.; Lobbia, G. G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. *Inorg. Chem.* **1998**, *37*, 890.
(4) Santini, C.; Pettinari, C.; Lobbia, G. G.; Spagna, R.; Pellei, M.; Vallorani, F. *Inorg. Chim. Acta* **1999**, *285*, 81.
(5) Reglinski, J.; Garner, M.; Cassidy, I. D.; Slavin, P. A.; Spicer, M. D.; Armstrong, D. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2119.
(6) Reglinski, J.; Spicer, M. D.; Garner, M.; Kennedy, A. R. *J. Am. Chem. Soc.* **1999**, *121*, 2317.
(7) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **1999**, 2301.
(8) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.
(9) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Hascall, T.; Parkin, G. *Inorg. Chem.* **2000**, *39*, 4240.
(10) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 891.
(11) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 1267.
(12) Slavin, P. A.; Reglinski, J.; Spicer, M. D.; Kennedy, A. R. *J. Chem. Soc., Dalton Trans.* **2000**, 239.
(13) Bridgewater, B. M.; Filleben, T.; Friesner, R. A.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4494.
(14) Trofimenko, S. *Scorpionates, the Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
(15) Paulo, A.; Domingos, A.; Garcia, R.; Santos, I. *Inorg. Chem.* **2000**, *39*, 5669 and references therein.
(16) (a) Garcia, R.; Paulo, A.; Domingo, A.; Santos, I.; Ortner, K.; Alberto, R. *J. Am. Chem. Soc.* **2000**, *122*, 11240. (b) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **2001**, *632*, 41.

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of preparing pure and water stable ^{99m}Tc complexes using very low ligand concentration. All these features highlighted the potential relevance of model compounds **1**−**4** as building blocks for the development of radiopharmaceuticals, namely for labeling biomolecules with ^{99m}Tc or $^{186/188}$Re. On the basis of model complexes **1**−**4**, several approaches can be used for the labeling of biomolecules.[16,17] For complexes [M{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (M = Re (**2a**), $^{99/99m}$Tc (**2b**)), which present an unprecedented agostic B−H···Tc interaction, one of these approaches relies on the cleavage of the agostic B−H···M interaction by neutral substrates (L), potentially able to be functionalized with biomolecules. An essential prerequisite to apply this approach is to find substrates strong enough to cleave the agostic interaction. In the search of adequate substrates, we have decided to investigate the possibility of adding different neutral ligands (imidazole (imzH), 4-(dimethylamino)pyridine (4-NMe$_2$py), *tert*-butylisonitrile (^{t}BuNC), triphenylphosphine (PPh$_3$), ethylenediamine (en), and 1,2-bis(diphenyl)phosphinoethane (dppe)) to complex [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**).

Herein, we report on the synthesis, characterization, and stability of the resulting mixed compounds [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(L)] (L = imzH (**5**), 4-NMe$_2$py (**6**), ^{t}BuNC (**7**), PPh$_3$ (**8**)), [Re{κ^1-H$_2$B(tim^{Me})$_2$}(CO)$_3$(en)] (**9**), and [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$]$_2$(μ-dppe) (**10**).

Experimental Section

General Procedures. The reactions were carried out under air, except when indicated to the contrary. Chemicals and solvents were of reagent grade and were used without further purification. [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**) was prepared as described previously.[16] ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H chemical shifts were referenced with the residual solvent resonances relative to tetramethylsilane, and the ^{31}P NMR chemical shifts with external 85% H$_3$PO$_4$ solution. NMR spectra were run in CD$_3$CN or in CDCl$_3$. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a EA110 CE Instruments automatic analyzer. Although all complexes were isolated with high chemical purity, as indicated by ^{1}H NMR, low values were systematically obtained for the hydrogen analysis.

Synthesis of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$(imzH)] (5). To a suspension of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**) (200 mg, 0.40 mmol) in toluene was added imzH (130 mg, 1.9 mmol). The reaction mixture was stirred for 24 h, and after this period of time, the solvent was removed under vacuum. After washing the residue with diethyl ether, to remove free imidazole, a white microcrystalline solid was recovered which has been formulated as **5** (140 mg, 0.24 mmol, η = 60%).

Anal. Calcd for $C_{14}H_{16}BN_6O_3ReS_2$: C, 29.12; H, 2.77; N, 14.67. Found: C, 29.57; H, 2.54; N, 14.67. IR(cm^{-1}): 1860, 1880, 1905 and 2000 (ν(CO)), 2400 and 2460 (ν(BH)). ^{1}H NMR (300 MHz, CD$_3$CN, δ (ppm)): 3.65 (s, 6H, CH$_3$), 6.92 (d, 2H, CH), 7.02 (d, 2H, CH), 7.10 (br, 1H, CH, imzH), 7.27 (br, 1H, CH, imzH), 8.09 (br, 1H, CH, imzH), 10.77 (s, 1H, NH, imzH).

Synthesis of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$(4-NMe$_2$py)] (6). Complex **6** was prepared and recovered as described for **5**. A 95 mg (0.15 mmol, η = 85%) portion of **6** in the form of a white microcrystalline solid was obtained by reacting 112 mg (0.22 mmol) of **2a** with excess (dimethylamino)pyridine (135 mg, 1.11 mmol).

Anal. Calcd for $C_{18}H_{22}BN_6O_3ReS_2$: C, 34.21; H, 3.48; N, 13.30. Found: C, 34.78; H, 2.27; N, 13.14. IR(cm^{-1}): 1865, 1880 and 2000 (ν(CO)), 2380 and 2460 (ν(BH)). ^{1}H NMR (300 MHz, CDCl$_3$, δ (ppm)): 3.02 (s, 6H, N−CH$_3$, py*), 3.75 (s, 6H, CH$_3$), 6.43 (d, 2H, *m*-py*), 6.73 (d, 2H, CH), 6.98 (d, 2H, CH), 8.52 (d, 2H, *o*-py*).

Synthesis of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$(^{t}BuNC)] (7). To a suspension of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**) (100 mg, 0.20 mmol) in toluene was added excess ^{t}BuNC (100 μL, 0.88 mmol), and the reaction mixture was stirred for 24 h. Compound **7** (100 mg, 0.17 mmol, η = 85%) was recovered as a white microcrystalline solid, after removal of the solvent under vacuum and washing with *n*-hexane.

Anal. Calcd for $C_{16}H_{21}BN_5O_3ReS_2$: C, 32.43; H, 3.55; N, 11.82. Found: C, 32.58; H, 3.30; N, 11.70. IR(cm^{-1}): 1890, 1950, and 2010 (ν(CO)); 2165 (ν(CN)); 2400 and 2460 (ν(BH)). ^{1}H NMR (300 MHz, CD$_3$CN, δ (ppm)): 1.31 (s, 9H, CH$_3$, ^{t}Bu), 3.69 (s, 6H, CH$_3$), 6.98 (d, 2H, CH), 7.07 (d, 2H, CH).

Synthesis of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$(PPh$_3$)] (8). Complex **8** was prepared and recovered as described for **5** and **6**. A 178 mg (0.23 mmol, η = 58%) portion of **8** in the form of a white microcrystalline solid was obtained by reacting 200 mg (0.40 mmol) of **2** with excess triphenylphosphine (510 mg, 1.95 mmol).

Anal. Calcd for $C_{29}H_{27}BN_4O_3PReS_2$: C, 45.10; H, 3.50; N, 7.26. Found: C, 45.10; H, 2.92; N, 6.83. IR(cm^{-1}): 1860, 1905 and 2000 (ν(CO)), 2380 and 2440 (ν(BH)). ^{1}H NMR (300 MHz, CDCl$_3$, δ (ppm)): 3.70 (s, 6H, CH$_3$), 6.69 (d, 2H, CH), 6.98 (d, 2H, CH), 7.32−7.42 (m, 9H, CH, *m*+*p*-Ph), 7.74 (m, 6H, CH; *o*-Ph). ^{31}P NMR (121.3 MHz, CDCl$_3$, δ (ppm)): 13.38.

Synthesis of [Re{κ^1-H$_2$B(tim^{Me})$_2$}(CO)$_3$(en)] (9). To a solution of compound **2a** (100 mg, 0.196 mmol) in methanol was added excess ethylenediamine (65 μL, 0.973 mmol). The resulting solution was heated under reflux for 2 h, precipitating a white solid. After this time, the reaction mixture was dried under vacuum, to remove the solvent and excess ethylenediamine. ^{1}H NMR analysis of the crude material revealed that it contained essentially complex **9**. Further purification of **9** was achieved by recrystallization from methanol. Yield: 70 mg (0.123 mmol, 63%).

Anal. Calcd for $C_{16}H_{21}BN_7O_3ReS_2$: C, 27.42; H, 3.51; N, 14.76. Found: C, 27.59; H, 2.16; N, 14.21. IR(cm^{-1}): 1880 and 2000 (ν(CO)), 2390 and 2430 (ν(BH)), 2990−3650 ((ν(NH)). ^{1}H NMR (300 MHz, CD$_3$CN, δ (ppm)): 2.72 (m, 2H, CH$_2$, en), 3.00 (m, 2H, CH$_2$, en), 3.43 (s, 3H, CH$_3$), 3.72 (s, 3H, CH$_3$), 4.10 (br, 4H, N−H, en), 6.63 (d, 1H, CH), 6.71 (d, 1H, CH), 6.93 (d, 1H, CH), 6.96 (d, 1H, CH).

Synthesis of [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$]$_2$(μ-dppe) (10). While under nitrogen, dppe (20 mg, 0.05 mmol) was added to a methanolic solution of compound **2a** (50 mg, 0.098 mmol). The reaction mixture was heated under reflux for 2 h, and while refluxing, complex **10** began to precipitate as a white microcrystalline solid. After cooling to room temperature, **10** was recovered by filtration, followed by washing with methanol (2 × 5 mL) and drying under vacuum. Yield: 46 mg (0.032 mmol, 58%).

Anal. Calcd for $C_{48}H_{48}B_2N_8O_6P_2Re_2S_4$: C, 40.68; H, 3.39; N, 7.91. Found: C, 40.35; H, 2.87; N, 7.67. IR(cm^{-1}): 1865, 1910 and 2000 (ν(CO)), 2400 and 2460 (ν(BH)). ^{1}H NMR (300 MHz, CDCl$_3$, δ (ppm)): 2.70 (s, 4H, CH$_2$, dppe), 3.66 (s, 12H, CH$_3$), 6.67 (d, 4H, CH), 6.94 (d, 4H, CH), 7.37 (br, 12H, *m*+*p*-Ph, dppe), 7.59 (br, 8H, *o*-Ph, dppe). ^{31}P NMR (121.3 MHz, CDCl$_3$, δ (ppm)): 7.79.

(17) Garcia, R.; Xing, Y. H.; Paulo, A.; Domingos, A.; Santos, I. Unpublished results.

Table 1. Crystallographic Data for **6** and **8**−**10**

	6	**8**	**9**	**10**
formula	$C_{18}H_{22}BN_6O_3S_2Re$	$C_{29}H_{27}BN_4O_3PS_2Re$	$C_{13}H_{18}BN_6O_3S_2Re$	$C_{48}H_{48}B_2N_8O_6PS_4Re_2{\cdot}2C_4H_8O$
mol wt	631.55	771.65	567.46	1561.36
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
space group	$Cmc2_1$	$Pbca$	$P\bar{1}$	$P2_1/n$
a, Å	29.462(3)	10.3595(4)	8.4512(7)	10.0319(12)
b, Å	14.386(2)	18.0988(12)	11.591(2)	13.517(3)
c, Å	17.546(2)	33.845(2)	11.980(2)	23.508(3)
α, deg			117.409(14)	
β, deg			98.312(14)	98.706(12)
γ, deg			94.345(14)	
V, Å^3	7437(2)	6345.8(6)	1017.2(3)	3151.0(9)
Z	12	8	2	2
ρ_{calcd}, g cm^{-3}	1.692	1.615	1.853	1.646
μ(Mo Kα), mm^{-1}	5.100	4.048	6.202	4.079
R1[a]	0.0652	0.0591	0.0252	0.0543
wR2[a]	0.0971	0.1020	0.0530	0.0808

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. The values were calculated for data with $I > 2\sigma(I)$ only.

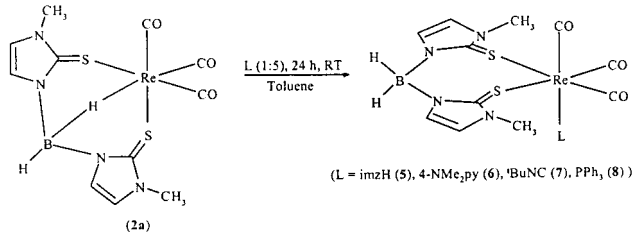
X-ray Crystallographic Analysis. X-ray data were collected from white crystals of **6** (0.31 × 0.22 × 0.16 mm^3), **8** (0.29 × 0.16 × 0.15 mm^3), **9** (0.63 × 0.14 × 0.09 mm^3), and **10** (0.45 × 0.22 × 0.18 mm^3). The crystals were obtained by recrystallization from THF/*n*-hexane (**6**, **8**, and **10**) or acetonitrile (**9**) and mounted in thin-walled glass capillaries. The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, using an $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $14.8° < 2\theta < 23.9°$ for **6**, $20.8° < 2\theta < 31.8°$ for **8**, $15.2° < 2\theta < 26.9°$ for **9**, and $15.3° < 2\theta < 25.7°$ for **10**. The crystal data are summarized in Table 1.

The data were corrected[18] for Lorentz polarization effects and for absorption (Ψ scans). The heavy atom positions were located by Patterson methods using SHELXS-86.[19] The remaining atoms were located by sucessive least-squares refinements on F^2 using SHELXL-93.[20] Complex **6** crystallizes with two independent molecules in the asymmetric unit. In one of these molecules, the Re and B atoms, one of the CO ligands, and the pyridine ligand lie on a plane of symmetry. The atoms from this pyridine ligand display large displacement parameters, and their refinement was performed with some geometrical constraints on distances and imposing a flat geometry for the ring. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters. For complex **10**, there are two molecules of THF of crystallization per formula unit. The contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon or boron atoms. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93.[20] The drawings were made with ORTEP-II[21a] and ORTEP-3,[21b] and all the calculations were performed on a Decalpha 3000 computer.

Results and Discussion

Syntheses. As we reported in a previous communication, the agostic B−H···M (M = Re, Tc) interaction in complexes

Scheme 1



2a and **2b** remains intact in most common coordinating solvents, such as alcohols, water, dimethyl sulfoxide, tetrahydrofuran, or acetonitrile.[16a] Despite this robustness, we anticipated that the finding of neutral substrates that break the B−H···M interaction, in a selective and efficient way, should allow the use of complexes **2a** and **2b** as preformed synthons for the labeling of biomolecules. Obviously, the choice and screen of adequate substrates should be focused on those with a well recognized affinity for the *fac*-[Re(CO)$_3$]$^+$ moiety and which offer the possibility of being functionalized with biomolecules. To get chemical information helpful in the choice of co-ligands for further functionalization with biomolecules, we have evaluated the reactivity of [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**) toward monodentate and potentially bidentate substrates such as imidazoles, pyridines, isonitriles, phosphines, and amines.

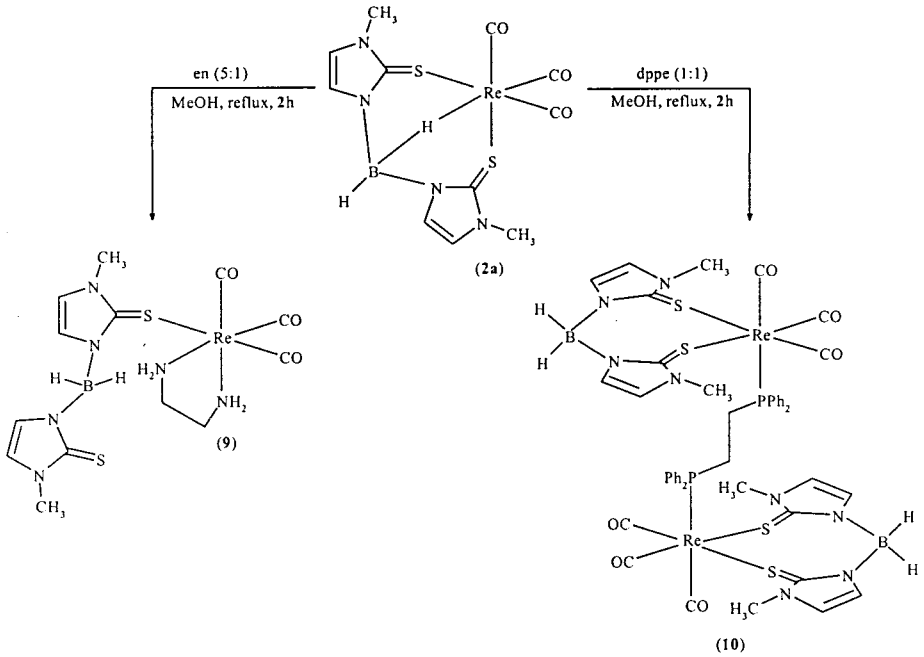
As indicated in Scheme 1, complex **2a** reacts with excess (1:5) of the monodentate neutral substrates leading to the novel mixed complexes [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(L)] (L = imzH (**5**), 4-NMe$_2$py (**6**), ^{t}BuNC (**7**), PPh$_3$ (**8**)).

In the reactions of **2a** with potentially bidentate ligands, such as ethylenediamine and 1,2-bis(diphenyl)phosphinoethane, a different reactivity was observed, and the compounds isolated were monomer [Re{κ^1-H$_2$B(tim^{Me})$_2$}(CO)$_3$(en)] (**9**) and dimer [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$]$_2$(μ-dppe) (**10**), respectively (Scheme 2).

Complexes **5**−**10** are white microcrystalline solids, which were obtained in moderate to high yield (60%−85%). Compounds **6**−**8** and **10** are highly soluble in most common polar organic solvents; **5** and **9** are only sparingly soluble in alcohols and halogenated hydrocarbons but highly soluble

(18) Fair, C. K. *MOLEN*; Enraf-Nonius: Delft, The Netherlands, 1990.
(19) Sheldrick, G. M., *SHELXS-86: Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1986.
(20) Sheldrick G. M. *SHELXL-93: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1993.
(21) (a) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (b) Farrugia, L. *J. Appl. Crystallogr.* **1997**, *32*, 565.

Scheme 2



in acetonitrile or dimethyl sulfoxide. All compounds are stable toward aerial oxidation and hydrolysis, either in solid state or in solution. However, with the exception of the isonitrile derivative (**7**), the adducts with monodentate ligands (**5**, **6**, **8**) tend to regenerate slowly starting compound [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2a**), if kept in solution without excess of the corresponding unidentate co-ligand (imidazole, pyridine, or phosphine). The follow-up of this process by ^{1}H NMR has shown that, after 24 h at room temperature, there is approximately a 50% conversion of complexes **3**, **4**, and **6** into **2a**, which is the unique species formed. In the case of *n*-butylamine, we could observe the formation of the compound [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(^{n}BuNH$_2$)] by reacting **2a** with this aliphatic amine and following the reaction by ^{1}H NMR spectroscopy. However, we were unable to isolate the mixed complex in the solid state because, after drying the reaction mixtures under vacuum, pure [Re{κ^3-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (**2**) was the only compound recovered. This can be explained by the rebuilding of the agostic B−H···Re interaction, concomitantly with the removal of the volatile amine, and it indicates a certain dynamic character for the process. In summary, these data indicate that the electronic properties of the unidentate co-ligand have a marked influence on the rebuilding of the agostic B−H···Re interaction. In complex **7**, the strong π-acceptor character of the *tert*-butylisonitrile ligand probably prevents such rebuilding.

Interestingly, the reaction of **2a** with ethylenediamine involves cleavage of the B−H···Re bond and replacement of one of the sulfur atoms by the second nitrogen of the diamine. The most probable intermediate is a species such as "[Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(κ^1-H$_2$NCH$_2$CH$_2$NH$_2$)]", which is analogous to the mixed complexes (**5**−**8**) discussed previously. However, we did not detect the formation of such an intermediate, even when the reaction was followed by ^{1}H NMR. Most probably, the rate limiting step of the process is the formation of such an intermediate that, when formed, is fast and irreversibly converted into complex **9**.

In contrast with ethylenediamine, the softer 1,2-bis(diphenyl)phosphinoethane is unable to replace the sulfur atoms of the dihydrobis(mercaptoimidazolyl)borate. There was no evidence for the formation of a monomer analogous to **8**, even when a large excess of diphosphine (5:1 molar ratio) was used. In the case of the reaction with dppe, the hypothetical intermediate "[Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(κ^1-Ph$_2$PCH$_2$CH$_2$PPh$_2$)]" is converted into [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$]$_2$(μ-dppe) (**10**), upon replacement of the B−H···Re bond in a second molecule of complex **2a**. The differences found in the coordination behavior of the potentially bidentate chelating ligands (en or dppe) must reflect electronic factors instead of stereochemical ones. The ability of the ethylenediamine ligand to coordinate in a bidentate fashion can be certainly accounted for by the enhanced hard character of the d^6 *fac*-[Re(CO)$_3$]$^+$ moiety, as a consequence of the strong π-acceptor properties of the carbonyl ligands. This enhanced hard character is well illustrated by the remarkable stability of different Re(I) tricarbonyl complexes containing relatively hard ligands with nitrogen (i.e., imidazole, amines) and oxygen donor atoms (i.e., carboxylate).[22]

Spectroscopic Data. The collected spectroscopic data (IR, ^{1}H and ^{31}P NMR) are consistent with the molecular structures of complexes **5**−**10**, which for some of them were confirmed by X-ray diffraction analysis.

The IR spectra of **5**−**10** display very strong ν(CO) bands, ranging from 1860 to 2010 cm^{-1}, with the typical pattern of complexes with the "*fac*-Re(CO)$_3$" moiety. In the spectrum of complex **7**, these frequencies are slightly blue-shifted in comparison with the ν(CO) bands in the IR spectra of the other complexes. A possible explanation for this trend is

(22) Alberto, A.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, A. P. *Coord. Chem. Rev.* **1999**, *190*−*192*, 901.

competition of the isonitrile in π-back-bonding with the metal, as previously invoked by other authors.[23] However, this is not corroborated by the ν(CN) stretching frequency (2165 cm^{-1}) observed for the coordinated *tert*-butylisonitrile in **7**, which is even higher than in free *tert*-butylisonitrile. Then, apparently, the isonitrile is acting mainly as a σ donor. The presence of two medium intensity bands in the range 2380−2460 cm^{-1} is another significant feature of the IR spectra of complexes **5**−**10**. These bands were attributed to the ν(B−H) stretching vibrations of the bidentate (**5**−**8** and **10**) or unidentate (**9**) dihydrobis(mercaptoimidazolyl)borate. Recently, it has been claimed that the ν(B−H) frequency can be an useful indicator of the hapticity of poly(pyrazolyl)-borates in coordination complexes of d-transition metals.[24] For the family of complexes herein described, the ν(B−H) frequencies observed for **9** ({κ^1-$H_2B(tim^{Me})_2$}) and for **5**−**8** and **10** ({κ^2-$H_2B(tim^{Me})_2$}) are not significantly different. However, so far, the number of complexes with this type of ligand is limited, with it being premature to correlate hapticity with the ν(B−H) frequencies.

The ^{1}H NMR spectra of complexes **5**−**8** and **10** display a set of two doublets due to the C−*H* protons of the 2-mercapto-1-methylimidazolyl rings and a unique singlet for the CH_3 groups of these rings. These data indicate that the two coordinated rings are magnetically equivalent, in agreement with the C_s symmetry of the complexes, which was confirmed for some of them (**6**, **8**, and **10**) by X-ray diffraction analysis. By contrast, in the ^{1}H NMR spectrum of [Re{κ^1-$H_2B(tim^{Me})_2$}$(CO)_3$(en)] (**9**), the protons from the mercaptoimidazolyl rings appear as a set of four doublets (C−*H* protons) and as a set of two singlets (CH_3 protons). This pattern is consistent with the presence of one coordinated mercaptoimidazolyl ring and a noncoordinated one, as confirmed in the solid-state molecular structure of **9** (see later). In the ^{1}H NMR spectra of complexes **5**−**10**, the resonances due to the protons of the correspondent unidentate co-ligands appear within the usual range of chemical shifts, displaying the expected splitting patterns. However, the spectrocopic data obtained for **9** and **10** justify some further comments. In CD_3CN, the ^{1}H NMR spectrum of [Re{κ^1-$H_2B(tim^{Me})_2$}$(CO)_3$(en)] (**9**) shows two multiplets of equal intensity for the methylenic protons of neutral and bidentate ethylenediamine. This is consistent with the diastereotopic character of these protons, which point either toward one of the CO ligands or toward the coordinated sulfur from the unidentate dihydrobis(mercaptoimidazolyl)borate, as confirmed by the X-ray diffraction analysis of **9** (see later). One would expect the same type of splitting for the N−H protons of ethylenediamine, but in CD_3CN, only one broad signal is observed at 4.10 ppm for these protons. Most probably, this is due to occasional overlapping of the two N−H resonances. In fact, in DMSO-d_6, two well separated signals at 5.32 and 4.37 ppm are observed for the N−H protons of ethylenediamine, confirming their diastereotopic character. However, DMSO-d_6 is not the solvent of choice to run the ^{1}H NMR spectra of **9**, as one of the resonances due to the methyl groups of the dihydrobis(mercaptoimidazolyl)borate is hidden by the residual water present in the solvent. For [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$]$_2$(μ-dppe) (**10**), only one singlet is observed for the methylenic protons of the diphosphine, in agreement with the centrosymmetric molecular structure of **10**, which was confirmed by X-ray diffraction analysis. Consistently, only one signal was observed in the ^{31}P NMR spectrum of **10**.

Table 2. Selected Bond Lengths and Angles for the Two Independent Molecules of **6**

Molecule 1

Distances (Å)			
av Re(1)−C	1.87(3)	av Re(1)−S	2.537(7)
Re(1)−N(1)	2.20(2)	av C−O	1.18(3)
av C−S	1.73(3)		

Angles (deg)			
C(1)−Re(1)−C(2)	89.1(13)	C(1)−Re(1)−C(3)	87.1(11)
C(2)−Re(1)−C(3)	89.5(4)	C(1)−Re(1)−N(1)	94.0(9)
C(1)−Re(1)−S(1)	91.8(10)	C(1)−Re(1)−S(2)	176.7(8)
C(2)−Re(1)−N(1)	93.9(9)	C(2)−Re(1)−S(1)	177.9(8)
C(2)−Re(1)−S(2)	92.3(9)	C(3)−Re(1)−N(1)	176.5(10)
C(3)−Re(1)−S(1)	92.5(8)	C(3)−Re(1)−S(2)	95.9(8)
N(1)−Re(1)−S(1)	84.1(5)	N(1)−Re(1)−S(2)	82.9(5)
S(1)−Re(1)−S(2)	86.7(2)		

Molecule 2

Distances (Å)			
av Re(2)−C	1.83(4)	Re(2)−S(3)	2.535(8)
Re(2)−N(7)	2.18(4)	av C−O	1.19(4)
C(19)−S(3)	1.64(3)		

Angles (deg)			
C(23)−Re(2)−C(24)	88.7(13)	C(24)−Re(2)−C(24′)[a]	86(2)
C(23)−Re(2)−N(7)	175(2)	C(23)−Re(2)−S(3)	95.9(8)
C(24)−Re(2)−N(7)	95.0(13)	C(24)−Re(2)−S(3)	91.6(11)
C(24)−Re(2)−S(3′)[a]	174.6(11)	N(7)−Re(2)−S(3)	80.6(7)
S(3)−Re(2)−S(3′)[a]	90.8(4)		

[a] Atoms related by the symmetry operation: $-x, y, z$.

Molecular Structures of Complexes 6, 8, 9, and **10.** Single-crystal X-ray diffraction analysis confirmed the identity of [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$(L)] (L = 4-NMe_2py (**6**), PPh_3 (**8**)), [Re{κ^1-$H_2B(tim^{Me})_2$}$(CO)_3$(en)] (**9**), and [Re-{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$]$_2$(μ-dppe) (**10**). The structures of the complexes consist of discrete mononuclear (**6**, **8**, and **9**) or dinuclear (**10**) units with the rhenium atoms in a distorted octahedral environment. The facial arrangement of the three carbonyl ligands is a common feature of all structures. Selected bond lengths and angles are presented in Tables 2−5, and ORTEP diagrams are shown in Figures 1−4.

The structures of complexes [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$-(L)] (L = 4-NMe_2py (**6**), PPh_3 (**8**)) are analogous to the structure of [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$(imzH)] (**5**), which was briefly reported in a previous communication.[16a] As can be seen in Figures 1 and 2, $[H_2B(tim^{Me})_2]^-$ is coordinated in a bidentate way through the two sulfur atoms, defining an eight-membered chelating ring and occupying two of the equatorial positions. The remaining coordination position is occupied by the 4-(dimethylamino)pyridine (**6**) or phosphine (**8**) co-ligands.

The X-ray diffraction analysis of [Re{κ^1-$H_2B(tim^{Me})_2$}-$(CO)_3$(en)] (**9**) confirmed the unidentate coordination of

(23) Spies, H.; Glaser, M.; Hahn, F. E.; Lügger, T.; Scheller, D. *Inorg. Chim. Acta* **1995**, *232*, 235.
(24) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

Table 3. Selected Bond Lengths and Angles for **8**

	Distances (Å)		
Re−C(1)	1.89(2)	Re−C(2)	1.88(2)
Re−C(3)	1.94(2)	Re−S(1)	2.544(3)
Re−S(2)	2.523(4)	Re−P	2.498(4)
C(1)−O(1)	1.17(2)	C(2)−O(2)	1.17(2)
C(3)−O(3)	1.14(2)	C(4)−S(1)	1.73(2)
C(8)−S(2)	1.727(14)		
	Angles (deg)		
C(1)−Re−C(2)	89.8(9)	C(1)−Re−C(3)	86.6(8)
C(2)−Re−C(3)	92.0(6)	C(1)−Re−P	92.5(6)
C(1)−Re−S(1)	176.3(6)	C(1)−Re−S(2)	95.4(6)
C(2)−Re−P	94.9(5)	C(2)−Re−S(1)	87.2(6)
C(2)−Re−S(2)	174.6(6)	C(3)−Re−P	173.0(4)
C(3)−Re−S(1)	91.3(5)	C(3)−Re−S(2)	89.9(4)
P−Re−S(1)	89.93(13)	P−Re−S(2)	83.29(13)
S(1)−Re−S(2)	87.65(13)		

Table 4. Selected Bond Lengths and Angles for **9**

	Distances (Å)		
Re−C(1)	1.910(5)	Re−C(2)	1.900(4)
Re−C(3)	1.891(5)	Re−S(1)	2.550(1)
Re−N(1)	2.206(4)	Re−N(2)	2.223(3)
C(1)−O(1)	1.145(6)	C(2)−O(2)	1.153(6)
C(3)−O(3)	1.158(6)	C(4)−S(1)	1.731(4)
C(8)−S(2)	1.702(4)		
	Angles (deg)		
C(1)−Re−C(2)	87.7(2)	C(1)−Re−C(3)	89.7(2)
C(2)−Re−C(3)	88.2(2)	C(1)−Re−N(1)	94.9(2)
C(1)−Re−S(1)	94.8(1)	C(1)−Re−N(2)	172.4(2)
C(2)−Re−N(1)	93.9(2)	C(2)−Re−S(1)	177.3(1)
C(2)−Re−N(2)	94.1(2)	C(3)−Re−N(1)	175.1(2)
C(3)−Re−S(1)	92.8(1)	C(3)−Re−N(2)	97.7(2)
N(1)−Re−S(1)	84.98(9)	N(1)−Re−N(2)	77.7(1)
N(2)−Re−S(1)	83.27(9)	N(3)−B−N(5)	108.1(4)

Table 5. Selected Bond Lengths and Angles for **10**

	Distances (Å)		
Re−C(1)	1.890(11)	Re−C(2)	1.922(11)
Re−C(3)	1.898(11)	Re−S(1)	2.551(3)
Re−S(2)	2.539(2)	Re−P	2.481(2)
C(1)−O(1)	1.159(11)	C(2)−O(2)	1.152(11)
C(3)−O(3)	1.156(11)	C(4)−S(1)	1.724(10)
C(8)−S(2)	1.728(10)		
	Angles (deg)		
C(1)−Re−C(2)	88.1(4)	C(1)−Re−C(3)	90.5(4)
C(2)−Re−C(3)	88.3(4)	C(1)−Re−P	91.4(3)
C(1)−Re−S(1)	176.3(3)	C(1)−Re−S(2)	88.6(3)
C(2)−Re−P	179.6(3)	C(2)−Re−S(1)	90.5(3)
C(2)−Re−S(2)	93.7(3)	C(3)−Re−P	91.8(3)
C(3)−Re−S(1)	92.9(3)	C(3)−Re−S(2)	177.8(3)
P−Re−S(1)	89.91(8)	P−Re−S(2)	86.20(8)
S(1)−Re−S(2)	88.04(9)		

$[H_2B(tim^{Me})_2]^-$ and the bidentate coordination of ethylenediamine (Figure 3).

Complex **9** is the unique example of a coordination complex having a dihydrobis(2-mercapto-1-methyl-imidazolyl)borate coordinated in a κ^1-S fashion. To the best of our knowledge, even for the much more studied poly(pyrazolyl)borates, the unidentate coordination mode is quite rare.[25,26] Ethylenediamine forms a five-membered [ReN(1)C(12)N(2)C(13)] chelating ring, which adopts a gauche configuration with twisting of the C(12)−C(13) bond in order to achieve an unstrained conformation. Within the chelating ring, the dihedral angle between planes [ReN(1)C(12)] and [ReN(2)C(13)] is 18.4°, which is smaller than the corresponding values (23.5°−29°) found in related complexes [ReBr(CO)$_3$(*N*,*N*,*N*′,*N*′-tetramethylene-1,2-diamine)] and [ReBr(CO)$_3$(N,N′-dimethylethane-1,2-diamine)]. However, the torsional angle of 54.1° across the C−C bond of

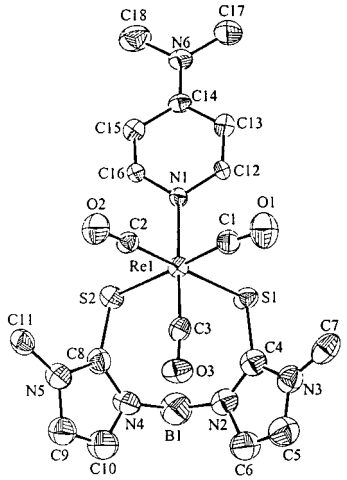


Figure 1. ORTEP view of [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(4-NMe$_2$py)] (**6**). Vibrational ellipsoids are drawn at the 30% probability level.

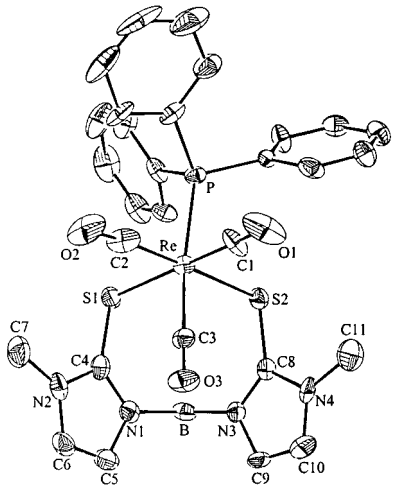


Figure 2. ORTEP view of [Re{κ^2-H$_2$B(tim^{Me})$_2$}(CO)$_3$(PPh$_3$)] (**8**). Vibrational ellipsoids are drawn at the 30% probability level.

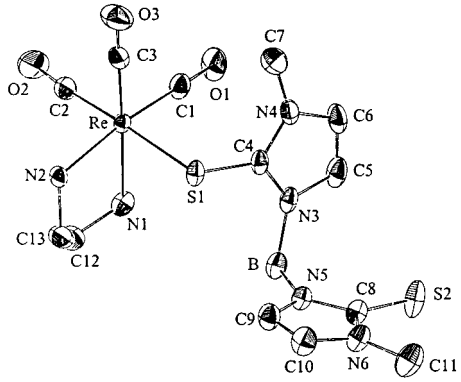


Figure 3. ORTEP view of [Re{κ^1-H$_2$B(tim^{Me})$_2$}(CO)$_3$(en)] (**9**). Vibrational ellipsoids are drawn at the 40% probability level.

(25) Gutiérrez, E.; Hudson, S. A.; Monge, A.; Nicasio, M. C.; Paneque, M.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1992**, 2651.
(26) Gutiérrez, E.; Hudson, S. A.; Monge, A.; Nicasio, M. C.; Paneque, M.; Ruiz, C. *J. Organomet. Chem.* **1998**, *551*, 215.

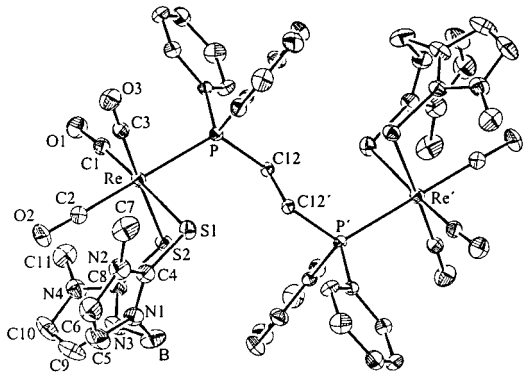


Figure 4. ORTEP view of [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$]$_2$(μ-dppe) (**10**). Vibrational ellipsoids are drawn at the 30% probability level.

ethylenediamine is within the range (51.4°−57.3°) previously reported for the latter complexes.[27,28]

The coordination environmental of each rhenium in dimeric [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$]$_2$(μ-dppe) (**10**) is identical to the one found for **8**, with the diphosphine bridging the two rhenium units. The dimeric structure of **10** contains an inversion center which makes each unit chemically and crystallographic equivalent (Figure 4).

In complexes **6**, **8**, **9**, and **10**, the Re−CO, Re−N, and Re−P bond lengths and the molecular parameters of the CO, pyridine, diamine, and phosphine ligands are normal, comparing with those found in previously described octahedral Re(I) tricarbonyl complexes with the *fac*-$[Re(CO)_3]^+$ moiety and containing this type of ligand.[27−32] Concerning bidentate $[H_2B(tim^{Me})_2]^-$, the mean values found for the Re−S distances are 2.536(8) Å in [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$(4-NMe_2py)] (**6**), 2.534(4) Å in [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_2$-(PPh_3)] (**8**), and 2.545(3) Å in [Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$]$_2$-(μ-dppe) (**10**). In complex [Re{κ^1-$H_2B(tim^{Me})_2$}$(CO)_3$(en)] (**9**), the Re−S bond distance for unidentate $[H_2B(tim^{Me})_2]^-$ (2.550(1) Å) is slightly larger than the average Re−S bond distances in monomeric **6** and **8**, reflecting the presence of eight-membered chelating rings in the later complexes. For **6** and **8**−**10**, the Re−S bond distances are larger than the values obtained for the precursor [Re{κ^3-H(μ-H)$B(tim^{Me})_2$}-$(CO)_3$] (**2**) (av Re−S of 2.508(1) Å).[16a] Most probably, this is justified by presence of the agostic B−H···Re interaction that obliges the ligand to assume a boat conformation with a closer approach to the Re(I) atom.

Concluding Remarks. We have shown that ligand $[H_2B(tim^{Me})_2]^-$ is very versatile toward the *fac*-$[Re(CO)_3]^+$ moiety. It can switch from tridentate (κ^3-HS_2) to bidentate (κ^2-S_2) or monodentate (κ^1-S), depending on the nature of the neutral co-ligands. For $\sigma + \pi$ donor co-ligands such as isonitriles, pyridines, imidazoles, or phosphines, disruption of the B−H···Re bond in [Re{κ^3-H(μ-H)$B(tim^{Me})_2$}$(CO)_3$] (**2a**) led to monomeric or dimeric complexes containing the fragment "Re{κ^2-$H_2B(tim^{Me})_2$}$(CO)_3$". By contrast, ethylenediamine, a harder and exclusive σ donor, tranforms **2a** into a mixed complex, [Re{κ^1-$H_2B(tim^{Me})_2$}$(CO)_3$(en)] (**9**), where the ligand displays the unprecedented κ^1-S coordination mode. The monomeric mixed complexes, **5**−**9**, are valuable models for the labeling of biomolecules. Attachment of the biomolecules to the incoming co-ligands enables an easy control of the physicochemical properties of the complexes, which are very important in targetting. Because of their enhanced stability in solution, the isonitrile and ethylenediamine derivatives, **7** and **9**, appear as the most promising for the development of specific ^{99m}Tc and $^{186/188}$Re radiopharmaceuticals.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **6**, **8**, **9**, and **10**. This material is available free via the Internet at http://pubs.acs.org.

IC011171N

(27) Couldwell, M. C.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1101.
(28) Abel, E. W.; Bhatti, M. M.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. A. *J. Organomet. Chem.* **1980**, *197*, 345.
(29) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem* **1989**, *28*, 1596.
(30) Yam, V. W. W.; Wong, K. M. C.; Lee, V. W. M.; Lo, K. W.; Cheung, K. K. *Organometallics* **1995**, *14*, 4034.
(31) Wallace, L.; Woods, C.; Rillema, D. P. *Inorg. Chem.* **1995**, *34*, 2875.
(32) Abram, U.; Alberto, R.; Dilworth, J. R.; Zheng, Y.; Ortner, K. *Polyhedron* **1999**, *18*, 2995.