Cationic Acetyl Complexes of Iron(II) and Ruthenium(II) Bearing Neutral N,O Ligands: Synthesis, Characterization, and Interionic Solution Structure by NOESY NMR Spectroscopy

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The reactions of complexes *trans, cis*-$M(PMe_3)_2(CO)_2(Me)I$ (M = Fe (**1a**), Ru (**1b**)) with N,O ligands [2-acetylpyridine (2-apy), 2-benzoylpyridine (2-bzpy), and 2,2′-dipyridyl ketone (2,2′-dpk)] in the presence of $NaBPh_4$ afford a mixture of the two possible stereoisomers *trans*-$[M(PMe_3)_2(CO)(COMe)(N, O)]BPh_4$ having the N arm cis (**A**) or trans (**B**) to the acetyl group. The stereochemistry of the complexes was determined by ^{1}H NOESY NMR spectra. For all the iron complexes the major stereoisomer is **B**, while for ruthenium complexes it is **A**. When **A**/**B** mixtures are left in methylene chloride, the concentration of **A** increases, indicating that **A** and **B** are the thermodynamic and kinetic reaction products, respectively. Furthermore, the more basic the N,O ligands, the more **B** stereoisomer that forms. The solid-state structure of **4b** was obtained using single-crystal X-ray diffraction. For all the complexes, the ion-pair structures and the localization of the counterion in solution with respect to the organometallic moiety were investigated by the detection of interionic contacts in the ^{1}H NOESY NMR spectra. Specific interactions were observed that indicate that the counterion is localized in solution in front of the face determined by PMe_3 and the two arms of the N,O ligands.

Introduction

There has recently been increased interest in complexes containing "hemilabile" N,O ligands because their hemilability can facilitate the coordination of a substrate into the coordination sphere of a transition metal.[1] Furthermore, in the case of neutral N,O ligands, the chelation of the O arm can stabilize reactive species. Cavell and co-workers demonstrated that Pd compounds containing N,O ligands can be used to isolate a reaction intermediate of the ethene insertion.[2]

Our interest in neutral N,O ligands is based on the above-mentioned properties and on two other reasons. First, during the kinetic studies on the migratory insertion of carbon monoxide in compounds *trans,cis*-$M(PMe_3)_2(CO)_2(Me)I$ (M = Fe (**1a**) Ru (**1b**)),[3] we realized that two processes can occur very easily: (1) the ionization of the M−I bond and (2) the migration of Me onto a cis CO. Depending on which process occurs first, it is possible to hypothesize two different reaction mechanisms (Scheme 1).

If both processes take place, two coordination sites are left free for the attack of a bidentate ligand.[4] Reactions with neutral N,O ligands, where the N arm is reasonably considered to be the first to coordinate to the metal, can give interesting information about the stereochemistry of the reaction and the active mechanism. Second, the reaction of neutral N,O ligands affords cationic complexes where all but the CO coordination sites around the metal contain nonequivalent protons. This makes the formed complexes suitable for studying their interionic structures in solution by detecting the interionic contacts in the ^{1}H NOESY spectra.[5]

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(1) For examples, see: (a) Canty, A. J.; Traill P. R.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **1997**, *255*, 117. (b) Frankcombe, K.; Cavell, K.; Knott, R.; Yates, B. *Chem. Commun.* **1996**, 781. (c) Jablonski, C.; Zhou, Z.; Bridson, J. *Inorg. Chim. Acta***1997**, *254*, 315. (d) Jin, H.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 2159. (e) Desjardins, S. Y.; Cavell, K. J.; Hoare, J. L.; Skelton, B. W.; Sobolev, A. N.; White, A. H.; Keim, W. *J. Organomet. Chem.* **1997**, *544*, 163. (f) Britovsek, G. J. P.; Cavell, K. J.; Green, M. J. Gerhards, F.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1997**, *533*, 201; Devenson, A. C.; Heath, S. L.; Harding, C. J.; Powell, A. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3173.

(2) Green, M. J.; Britovsek, G. J. P.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 1563.

(3) (a) Reichenbach, G.; Cardaci, G.; Bellachioma, G.; *J. Chem. Soc., Dalton Trans.* **1982**, 847. (b) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Madami, A. *Inorg. Chem.* **1993**, *32*, 554. (c) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *Inorg. Chem.* **1992**, *31*, 3018. (d) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *J. Organomet. Chem.* **1992**, *427*, C37.

(4) (a) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Gramlich, V.; Rüegger, H.; Terenzi, S.; Venanzi, L. M. *Organometallics*, **1997**, *16*, 2139. (b) Bellachioma, G.; Cardaci, G.; Gramlich, V.; Macchioni, A.; Pieroni, F.; Venanzi, L. M. *J. Chem. Soc., Dalton Trans.* **1998**, 947.

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Scheme 1

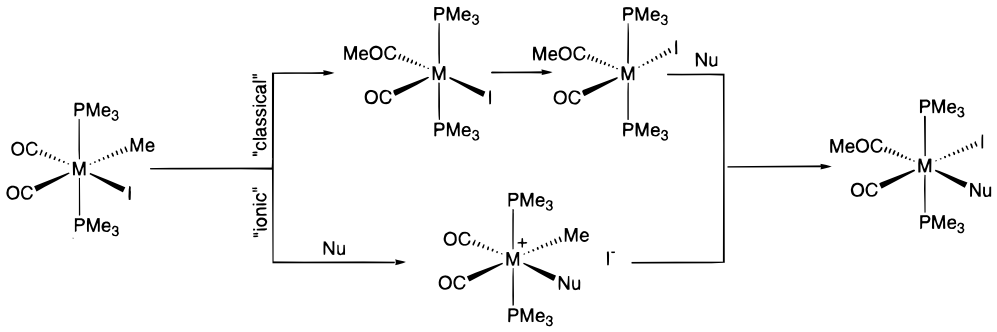
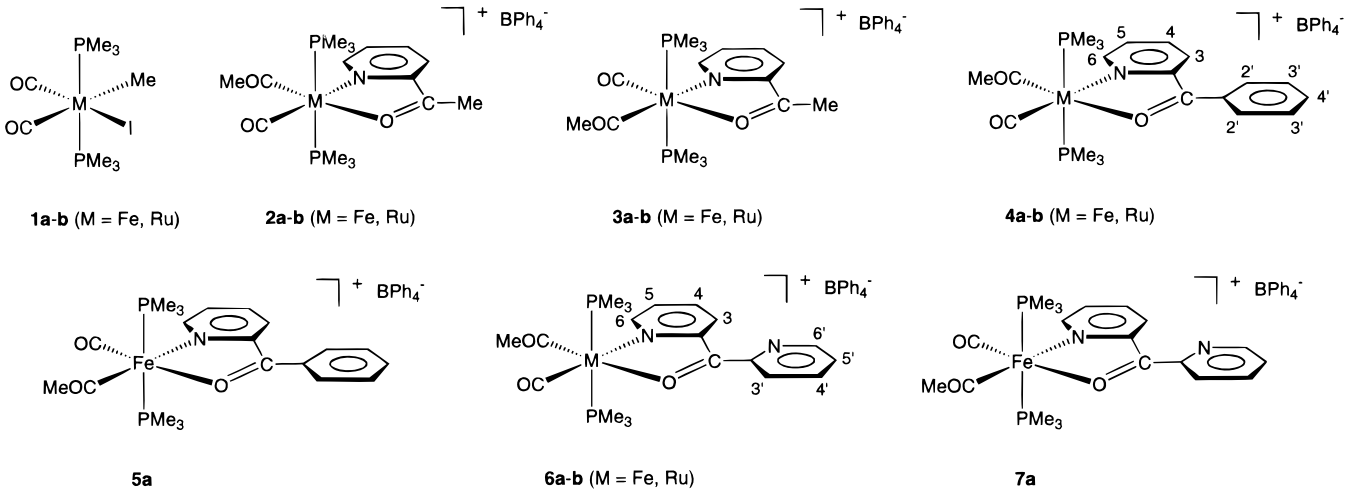


Chart 1



1a-b (M = Fe, Ru) **2a-b** (M = Fe, Ru) **3a-b** (M = Fe, Ru) **4a-b** (M = Fe, Ru)

5a **6a-b** (M = Fe, Ru) **7a**

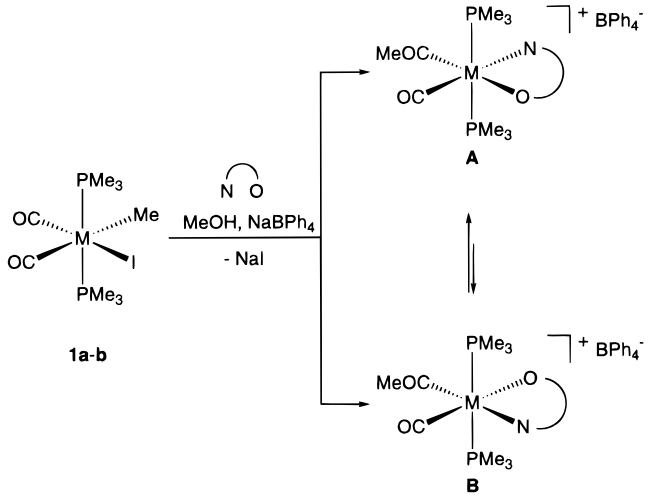
Here we report the results of our studies on the reactivity of complexes **1a**,**b** with several N,O ligands that allowed the new complexes **2**−**7**, shown in Chart 1, to be synthesized and the previously reported methodology, based on the nuclear Overhauser effect, has been extended to investigate the ion-pair solution structures of organometallic complexes.

Results and Discussion

Synthesis and Reactivity. The reactions of **1a**,**b** with N,O ligands in the presence of $NaBPh_4$ afford the acetyl complexes **2**−**7** according to Scheme 2.

All ruthenium compounds are dark red, stable in solid state, and relatively stable in solution, while iron compounds are violet and stable only in the solid state. In solution at room temperature they start to decompose after ca. 5 h. It is interesting to outline that in the case of the 2,2′-dpk ligand, where there is the possibility of the coordination of the N,N arms, we also observe the

Scheme 2



1a-b **A** **B**

coordination of the N,O arms. For all ligands, a mixture of two stereoismers **A** and **B** forms in a ratio that is strongly affected by the metal: **A** is the preferred stereoisomer for ruthenium, while **B** is favored in the case of iron compounds. Leaving complexes in CH_2Cl_2 solution, the concentration of stereoisomer **A** increases in both iron and ruthenium compounds. The ratios of the two stereoisomers, as soon as they are dissolved in CD_2Cl_2 and after ca. 6 h (evaluated by the integration of ^1H and ^{31}P NMR resonances) are reported in Table 1. This results can be explained by considering that **B** and **A** are the kinetic and thermodynamic reaction products, respectively. It is difficult to establish the active mechanism because for both mechanisms shown

(5) (a) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Terenzi, S. *Organometallics* **1996**, *15*, 4349. (b) For references on interionic studies of organic salts which catalyze phase-transfer reactions, see: (b) Pochapsky, T. C.; Wang, A.-P.; Stone, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 11084. (c) Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 6714. (d) Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 1460. For references on interionic studies of organolithium ion pairs, see: (e) Hoffman, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208. (f) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103. (g) Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 552. (h) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. (i) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.

Table 1. Ratios of the Two Stereoisomers A and B (A/B) in CD_2Cl_2 Determined by NMR Spectra

	M = Fe		M = Ru	
N,O ligand		after ca. 6 h		after ca. 20 h
2-apy	1/9	1/3	1/1	10/1
2-bzpy	1/8	1/3	only **A**	only **A**
2, 2'-dpk	1/5	1/4	only **A**	only **A**

Table 2. Experimental Data for X-ray Diffraction Study of 4b

empirical formula	$C_{45}H_{50}BNO_3P_2Ru$
mol wt	826.7
temperature (K)	293
system	monoclinic
space group	$P2_1/c$
a (Å)	15.46(2)
b (Å)	15.259(13)
c (Å)	18.09(2)
β (deg)	100.70(9)
V (Å^3)	4193(7)
Z	4
F(000)	1720
λ(Mo Kα) (Å)	0.710 73
μ(Mo Kα) (mm^{-1})	0.49
ϑ-range (deg)	1.8−20.0
index ranges	$0 \le h \le 14$, $0 \le k \le 14$, $-17 \le l \le 17$
no. of measd reflcns	4113
no. of unique reflcns used in the refinement	3923
no. of refined params	485
GOF on F^2	0.918
R_1 (on F, $I > 2\sigma(I)$	0.039
wR_2 (on F^2)	0.099

in Scheme 1 the nucleophile (in this case the N arm of the N,O ligands) occupies the position trans to the COMe group at the end of the reaction.[6] This means that in both mechanisms **B** is the kinetic reaction product. However, previous studies suggest that in the case of iron, the ionic mechanism is more probable than in ruthenium.[6] Furthermore, the reactivity of ruthenium is about 10 times higher than that of iron;[6e] this explains the greater amount of stereoisomer **A** in ruthenium compounds. Several synthesis carried out at 233 K demonstrated that the same preferential ratios remain.

There is also a slight dependence of the **A**/**B** ratios on the type of N,O ligand (see Table 2), particularly evident in the reaction of compound **1b** with 2-apy. This is the only case where stereoisomer **B** forms significantly with ruthenium and may be due to the better donor capacity of the oxygen of the ligand that partially slows down the isomerization process.

Characterization and Structure. (a) Solid State. X-ray crystallographic studies of **4b** were carried out. An ORTEP plot of **4b** is shown in Figure 1. Tables 2 and 3 show experimental parameters and a list of selected bond lengths and angles, respectively. The geometry at ruthenium in this complex is approximately octahedral. The Ru−O(3) separation is substantially elongated (2.226(4) Å) compared to similar compounds[2,7]

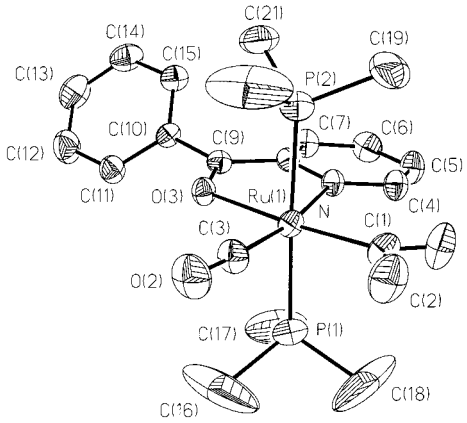


Figure 1. ORTEP view of cationic fragment of **4b**.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4b

Ru−P(1)	2.364(3)	C(3)−O(2)	1.141(6)
Ru−P(2)	2.360(3)	N−C(4)	1.331(6)
Ru−N	2.198(4)	N−C(8)	1.368(6)
Ru−O(3)	2.226(4)	C(8)−C(9)	1.470(7)
Ru−C(1)	2.014(6)	C(9)−O(3)	1.243(6)
Ru−C(3)	1.832(6)	C(9)−C(10)	1.478(7)
C(1)−O(1)	1.183(7)		
P(2)−Ru−P(1)	177.34(6)	P(2)−Ru−C(1)	88.7(2)
P(1)−Ru−O(3)	91.12(12)	P(2)−Ru−C(3)	90.6(2)
P(1)−Ru−N	89.09(13)	C(1)−Ru−C(3)	91.5(3)
P(2)−Ru−O(3)	90.28(12)	O(3)−Ru−C(3)	95.0(2)
P(2)−Ru−N	89.15(13)	N−Ru−C(1)	100.2(2)
Ru−N−C(8)	115.7(3)	O(3)−Ru−C(1)	173.4(2)
C(9)−C(8)−N	114.8(4)	N−Ru−C(3)	168.3(2)
O(3)−C(9)−C(8)	118.3(4)	Ru−C(3)−O(2)	176.6(5)
Ru−O(3)−C(9)	117.2(3)	C(9)−C(10)−C(11)	117.7(5)
P(1)−Ru−C(1)	89.6(2)	O(3)−C(9)−C(10)	118.8(5)
P(1)−Ru−C(3)	91.5(2)	O(3)−Ru−N	73.3(2)

because in trans position of O(3) there is the COMe group that it is known to exert a high trans-effect.[6a] Due to O(3) coordination to the ruthenium, the double bond C(9)−O(3) (1.243(6) Å) is weakened and is longer than the C(1)−O(1) bond (1.183(7) Å) but agrees with the usually reported values.[2,7] The five-member ring containing Ru−O(3)−C(9)−C(8)−N atoms is approximately coplanar with the equatorial ligands. There is however a remarkable deviation from the coplanarity between the phenyl group and the above-mentioned five-member ring. The angle between the least-squares planes through them is 43.4°. Other bond distances and angles fall within expected ranges for compounds of this type. The counterion is positioned close to the CO and O arm of the N,O ligand. Interionic distances can be evaluated by adding hydrogens to carbon atoms using standard values. The more important contacts are as follows: PMe_3, *p*-H, 2.74 Å; H-2′ and H-3′, *m*-H and *p*-H (3.4−4.0 Å).

(b) Solutions. Intramolecular Structure. Characterization of complexes **2**−**7** in this phase was carried out by IR and ^{1}H, ^{13}C, and ^{31}P NMR. The IR spectra of complexes show two bands in the carbonyl stretching region. The first, due to the COMe ligands, is metal-insensitive and falls close to 1600 cm^{-1} and the second, ν(CO), is at 1955 and 1935 cm^{-1} for the ruthenium and iron complexes, respectively, and shows the typical

(6) (a) Jablonski, C. R.; Wang, Y.-P. *Inorg. Chem.* **1982**, *21*, 4037. (b) Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936. (c) Cardaci, G.; Reichenbach, G.; Bellachioma, G.; Wassink, B.; Baird, M. C. *Organometallics* **1988**, *7*, 2475. (d) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Foresti, E.; Sabatino, P. *J. Organomet. Chem.* **1997**, *531*, 227. (e) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *J. Organomet. Chem.* **1997**, *540*, 7. (f) Aubert, M.; Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Burla, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 1759.

(7) (a) Bacchi, A.; Carcelli, M.; Costa, M.; Pelagatti, P.; Pelizzi, C.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1996**, 4239. (b) Sommerer, S.; Jensen, W. P. *Inorg. Chim. Acta* **1990**, *172*, 3.

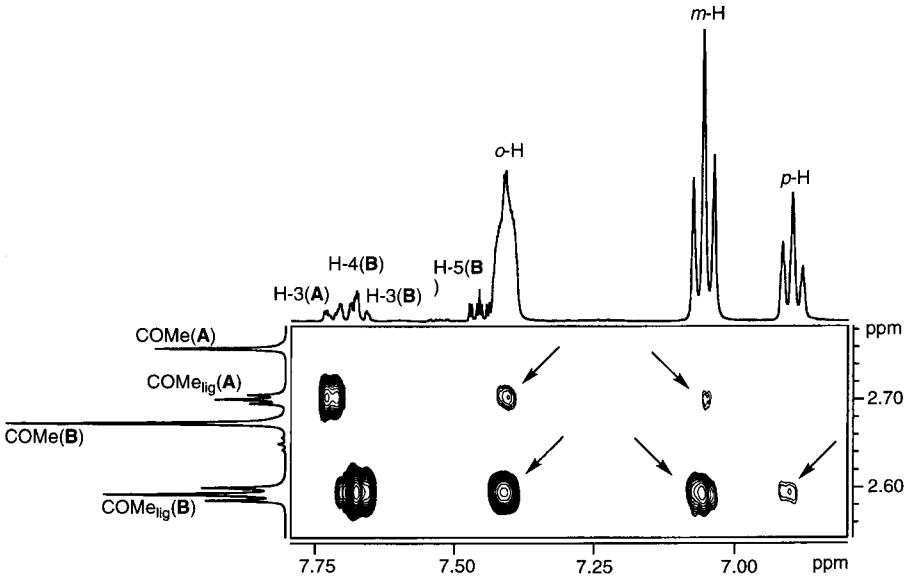


Figure 2. Section of ^{1}H NOESY spectrum of **2a** (**A**) and **3a** (**B**), recorded at 400.13 MHz in CD_2Cl_2, showing the interionic contacts between the COMe groups of the ligands and *o*-H and *p*-H protons.

difference of 20 cm^{-1}.[8] The C═O stretching band relative to the N,O ligands falls below 1600 cm^{-1}, and it was not clearly identified.

The assignment of the proton resonances in different fragments was obtained by combining information from ^{1}H COSY and ^{1}H NOESY NMR experiments. The latter experiments also provided the stereochemistry of the formed isomers. In the case of stereoisomer **A**, a contact between H-6 proton (see numeration reported in Chart 1) and the COMe protons was observed. Stereoisomer **B** can be identified by the absence of such a contact or directly from a contact between the COMe, H-2′, or H-3′ protons of the N,O ligand and the COMe proton for complexes **3a**,**b**, **5a**, or **7a**, respectively. As a further confirmation of the double bond character of the C═O bond in coordinated N,O ligands, $\delta_{CO_{lig}}$ falls close to 200 ppm.

Interionic Structures. In previous studies[4,5a] we showed that it is possible to localize the position of the counterion in solution by the detection of interionic contacts, in ^{1}H NOESY spectra, between protons belonging to it and some of the "organometallic" protons. In weak polar solvents (like methylene chloride), where only intimate ion pairs are present, we observed specific counterion-cation interactions for iron and ruthenium compounds[4] similar to those here reported having a N,N instead of N,O bidentate ligands. To see whether compounds **2**−**7** in methylene chloride solution also present specific anion−cation interactions and, consequently, extend the methodology, we recorded the phase-sensitive ^{1}H NOESY spectra for all of them. Specific interionic contacts were observed. In particular:

Complexes 2a and 3a. *o*-H and *m*-H of BPh_4^- show contacts with COMe of the ligand (see Figure 2) and H-4. PMe_3 protons show contacts with all three types of counterion protons.

Complexes 2b and 3b. *o*-H of BPh_4^- show contacts with COMe of the ligand. The protons of the PMe_3 groups interact with all the protons of BPh_4.

Complexes 4a and 5a. The PMe_3 protons show contacts with *o*-H and *m*-H, and H-4 and H-5 with *o*-H and *m*-H, respectively.

Complex 4b. H-5, H-4, and one of the H-2′ show contacts with *o*-H of BPh_4^-. The protons of the PMe_3 groups show strong contacts with all the protons of BPh_4^-.

Complexes 6a and 7a. There are strong contacts among the *o*-H, *m*-H, and *p*-H of BPh_4^- and all the protons of the ligand. The protons of the PMe_3 groups interact with all the protons of the BPh_4^-.

Complex 6b. *o*-H, *m*-H, and *p*-H of BPh_4^- show contacts only with the protons of PMe_3 groups; there are weak contacts among the *o*-H and *m*-H of BPh_4^- and the protons of the ligand.

For all complexes, BPh_4^- is specifically localized in front of the face determined by PMe_3 and both arms of the N,O ligands. As a confirmation of the specificity of the contacts, we never observed the interionic contact between the counterion and M-COMe protons. This agrees with quantomechanical and molecular mechanic calculations, recently carried out by us on analogous compounds containing N,N ligands,[9] that indicate a nonspherical distribution of the positive charge. In particular, the positive charge is partially delocalized on the rings of N,N ligands, while some negative charge is accumulated on the COMe group directly bonded to the metal. Furthermore, owing to the presence in N,N and N,O ligands of at least one aromatic ring, there is also an energetic gain from the van der Waals point of view for the counterion to stay close to such ligands.

The interionic structure of complex **4b** determined by single-crystal X-ray studies, presents the counterion between the CO and O arm of the N,O bidentate ligand. This means that the counterion position is slightly different than that found in solution where we also observed contacts between *o*-H and protons belonging to the pyridyl ring.

(8) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(9) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Cruciani, G.; Foresti, E.; Sabatino, P.; Zuccaccia, C. *Organometallics*, in press.

Conclusions

Cationic acetyl complexes **2**−**7** have been synthesized from the reaction of hemilabile N,O ligands with compounds **1a**,**b** and their stereochemistry has been determined by phase-sensitive ^{1}H NOESY NMR spectroscopy. Stereoisomers **A** and **B**, preferentially formed for ruthenium and iron, respectively, represent the thermodynamic and kinetic reaction products.

The interionic structure of complexes, investigated in CD_2Cl_2 by the NOESY NMR spectroscopy, indicates that the counterion is specifically localized in front of the face determined by PMe_3 and the two arms of the N,O ligands.

Experimental Section

General Data. Complexes **1a** and **1b** were prepared according to the literature.[3a,b] Reactions were carried out in a dried apparatus under a dry inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified prior to use by conventional methods.[10] All the ligands were purchased by Fluka and utilized without further purification.

IR spectra were taken on a 1725 X FTIR Perkin-Elmer spectrophotometer. One and two-dimensional ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS and external 85% H_3PO_4. NMR samples were prepared dissolving about 20 mg of compound in 0.5 mL of CD_2Cl_2, bubbling for 5 min with dried nitrogen. Two-dimensional ^{1}H NOESY spectra were measured with a mixing time of 800 ms.

X-ray Crystallography. Crystals of **4b**, suitable for single-crystal X-ray analysis, were obtained from CH_2Cl_2/ether/*n*-hexane. Diffraction intensities were collected at room temperature by the $\theta/2\theta$ scan method on a graphite monochromatized Syntex P21 diffractometer and reduced to F_o^2 values. The structure was solved by Patterson methods and refined by full-matrix least-squares calculations. For all computations, the SHELXTL package of crystallographic programs was used. Thermal vibrations were treated anisotropically for all non-H atoms. All H atoms were positioned geometrically (C−H 0.96 Å) and refined with adequate constraints. Final difference Fourier maps showed residual peaks lower than 1.3 e Å^{-3} in the proximity of the Ru atom.

Preparation of *trans*-[Fe(PMe$_3$)$_2$(CO)(COMe)(2-apy)]-BPh$_4$ (2a and 3a). **1a** (200 mg, 0.49 mmol) was dissolved in 8 mL of CH_3OH, and $NaBPh_4$ (large excess) was added. 2-Acetylpyridine (77 mg, 0.64 mmol) was slowly added. Immediately a reddish solid precipitated. The solution was stirred for an hour. The solid was filtered, washed with cold CH_3OH, and dried. The solid is a mixture of **2a** and **3a** in a ratio 1:9 (230 mg, yield 65%). Anal. Calcd (found) for $C_{40}H_{49}BFeO_3NP_2$: H, 1.92 (1.95); C, 62.57 (66.76); N, 6.29 (6.68). IR (CH_2Cl_2): ν_{CO} 1937 cm^{-1}; ν_{COMe} 1598 cm^{-1}. Complex **2a**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 10.25 (dddt, $^3J_{HH}$ = 5.6, $^4J_{HH} \approx {}^4J_{HP}$ = 1.6, $^5J_{HH}$ = 0.7, H-6), 7.88 (td, $^3J_{HH} = {}^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.7, H-4), 7.82 (td, $^3J_{HH} \approx {}^3J_{HH}$ = 5.5, $^4J_{HH}$ = 1.6, H-5), 7.72 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 0.8, H-3), 7.41 (m, *o*-H), 7.05 (t, $^3J_{HH} = {}^3J_{HH}$ = 7.3 *m*-H), 6.89 (t, $^3J_{HH}$ = 7.2 *p*-H), 2.60 (t, $^5J_{HP}$ = 1.9, COMe of the ligand), 2.54 (s, COMe), 0.99 (Harris t,[11] $|^2J_{PH} + {}^4J_{PH}|$ = 8.3, PMe_3). ^{31}P{^{1}H} NMR: 14.6 (s, PMe_3). ^{13}C{^{1}H} NMR: 274.8 (br, *C*OMe), 220.2 (t, $^2J_{CP}$ = 30.1, CO), 207.6 (s, *C*OMe$_{lig}$), 164.4 (q, $^1J_{BC}$ = 49.1, C-*ipso*), 154.8 (s, C-2), 149.2 (s, C-6), 140.3 (s, C-5), 136.3 (s, *o*-C), 130.6 (s, C-4), 129.7 (s, C-3), 126.2 (s, *m*-C), 122.3 (s, *p*-C), 50.8 (s, CO*Me*), 26.1 (s, CO*Me*$_{lig}$), 13.3 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 26.2, PMe_3). Complex **3a**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 8.75 (ddtd, $^3J_{HH}$ = 5.2, $^4J_{HH} \approx {}^5J_{HH} \approx {}^4J_{HP}$ = 0.5, H-6), 7.70 (m, H-4 AB system), 7.67 (m, H-3 AB system), 7.46 (ddd, $^3J_{HH} = {}^3J_{HH}$ = 5.3, $^4J_{HH}$ = 1.7, H-5), 7.41 (m, *o*-H), 7.05 (t, $^3J_{HH} = {}^3J_{HH}$ = 7.3 *m*-H), 6.89 (t, $^3J_{HH}$ = 7.2 *p*-H), 2.71 (t, $^5J_{HP}$ = 2.9 COMe of the ligand), 2.63 (s, COMe), 1.04 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 8.3, PMe_3). ^{31}P{^{1}H} NMR: 15.8 (s, PMe_3). ^{13}C{^{1}H} NMR: 276.7 (br, *C*OMe), 217.9 (t, $^2J_{CP}$ = 30.1, CO), 206.4 (t, $^4J_{CP}$ = 3.8 *C*OMe$_{lig}$), 164.4 (q, $^1J_{BC}$ = 49.1, C-*ipso*), 153.1 (s, C-2), 150.7 (s, C-6), 139.5 (s, C-5), 136.3 (s, *o*-C), 131.1 (s, C-4 and C-3), 126.2 (s, *m*-C), 122.3 (s, *p*-C), 49.7 (s, CO*Me*), 25.8 (t, $^4J_{CP}$ = 5.0 CO*Me*$_{lig}$), 13.4 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 27.3, PMe_3).

Preparation of *trans*-[Fe(PMe$_3$)$_2$(CO)(COMe)(2−bzpy)]-BPh$_4$ (4a and 5a). The procedure was the same as that for **2a** and **3a**. The solid is a mixture of **4a** and **5a** in a ratio 1:8 (yield 70%). IR (CH_2Cl_2): ν_{CO} 1943 cm^{-1}; ν_{COMe} 1597 cm^{-1}. Complex **4a**: ^{1}H NMR (in CD_2Cl_2, 294 K, *J* values in Hz): δ 10.33 (d, $^3J_{HH}$ = 5.5, H-6), 8.18 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.2, H-3), 2.58 (s, COMe), 1.01 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 8.4, PMe_3). ^{31}P{^{1}H} NMR: 17.3 (s, PMe_3). ^{13}C{^{1}H} NMR: 275.9 (t, *C*OMe), 220.0 (t, $^2J_{CP}$ = 29.4, CO), 202.3 (s, *C*OPh), 136.4 (s, *o*-C), 126.0 (s, *m*-C), 122.2 (s, *p*-C), 49.4 (s, CO*Me*). Complex **5a**: ^{1}H NMR (in CD_2Cl_2, 294 K, *J* values in Hz): δ 8.85 (d, $^3J_{HH}$ = 5.2, H-6), 8.22 (d, $^3J_{HH}$ = 8.0, H-3), 7.85 (d, $^3J_{HH}$ = 6.8, H-2′), 7.79 (t, $^3J_{HH}$ = 8.4, H-4′), 7.68 (t, $^3J_{HH}$ = 7.8, H-3′), 7.64 (d, $^3J_{HH}$ = 7.6, H-4), 7.44 (ddd, $^3J_{HH}$ = 6.8, $^3J_{HH}$ = 5.2, $^4J_{HH}$ = 1.2, H-5), 7.33 (m, *o*-H), 6.99 (t, $^3J_{HH}$ = 7.2, *m*-H), 6.84 (t, $^3J_{HH}$ = 7.2, *p*-H), 2.69 (s, COMe), 1.05 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 8.4, PMe_3). ^{31}P-{^{1}H} NMR: 18.8 (s, PMe_3). ^{13}C{^{1}H} NMR: 273.3 (br, *C*OMe), 217.9 (t, $^2J_{CP}$ = 31.1, CO), 199.6 (t, $^3J_{CP}$ = 4.3, *C*OPh), 164.5 (q, $^1J_{BC}$ = 49.4, C-*ipso*), 155.4 (s, C-2), 153.9 (s, C-6), 139.8 (s, C-1′), 139.1 (s, C-3), 136.4 (s, *o*-C), 136.1 (s, C-4), 133.2 (s, C-2′), 130.5 (s, C-4′), 130.2 (s, C-3′), 129.8 (s, C-5), 126.0 (s, *m*-C), 122.2 (s, *p*-C), 42.6 (s, CO*Me*), 13.6 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 13.4, PMe_3).

Preparation of *trans*-[Fe(PMe$_3$)$_2$(CO)(COMe)(2,2′-dpk)]-BPh$_4$ (6a and 7a). The procedure was the same as that for **2a** and **3a**. The solid is a mixture of **6a** and **7a** in a ratio 1:5 (yield 68%). IR (CH_2Cl_2): ν_{CO} 1944 cm^{-1}; ν_{COMe} 1599 cm^{-1}. Complex **6a**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 10.32(d, $^3J_{HH}$ = 4.0, H-6), 9.94 (d, $^3J_{HH}$ = 7.9, H-3), 8.83 (d, $^3J_{HH}$ = 4.5, H-6′), 8.24 (d, $^3J_{HH}$ = 7.9, H-3′), 8.15 (m, H-4′), 8.00 (td, $^3J_{HH}$ = 5.5, $^4J_{HH}$ = 1.2, H-4), 7.91 (m,H-5), 7.65 (m, H-5′), 7.33 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7.3, *m*-H), 6.90 (t, $^3J_{HH}$ = 7.1, *p*-H), 2.63 (s, COMe), 1.02 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 8.4, PMe_3). ^{31}P{^{1}H} NMR: 15.0 (s, PMe_3). ^{13}C{^{1}H} NMR: 268.1 (s, *C*OMe), 215.0 (s, CO), 163.7 (q, $^1J_{BC}$ = 49.3, C-*ipso*), 153.7 (s, C-6), 150.7 (s, C-2), 150.3 (s, C-2′), 149.3 (s, C-6′), 138.8 (s, C-5), 138.0 (s, C-5′), 135.6 (s, *o*-C), 134.2 (s, C-3), 129.7 (s, C-3′), 128.5 (s, C-4), 125.9 (s, C-4′), 125.4 (s, *m*-C), 121.6 (s, *p*-C), 48.9 (s, CO*Me*), 12.5 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 25.9, PMe_3). Complex **7a**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 10.07 (d, $^3J_{HH}$ = 8.1, H-3), 8.92 (d, $^3J_{HH}$ = 5.3, H-6), 8.88 (d, $^3J_{HH}$ = 4.2, H-6′), 8.47 (d, $^3J_{HH}$ = 7.9, H-3′) 8.09 (t, $^3J_{HH}$ = 5.2,H-4′), 7.99 (t, $^3J_{HH}$ = 5.4,H-4), 7.72 (t, $^3J_{HH}$ = 7.9, H-5′), 7.55 (t, $^3J_{HH}$ = 6.1, H-5), 7.33 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7.3, *m*-H), 6.90 (t, $^3J_{HH}$ = 7.1, *p*-H), 2.75 (s, COMe), 1.06 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 8.5, PMe_3). ^{31}P{^{1}H} NMR: 16.9 (s, PMe_3). ^{13}C{^{1}H} NMR: 272.7 (s, *C*OMe), 217.8 (s, CO), 163.7 (q, $^1J_{BC}$ = 49.3, C-*ipso*), 152.6 (s, C-6), 150.6 (s, C-2), 150.3 (s, C-2′), 149.7 (s, C-6′), 138.3 (s, C-5), 137.9 (s, C-5′), 136.0 (s, C-3), 135.6 (s, *o*-C), 130.2 (s, C-3′), 129.2 (s, C-4), 126.2(s, C-4′), 125.4 (s, *m*-C), 121.6 (s, *p*-C), 42.5 (s, CO*Me*), 12.8 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 27.5, PMe_3).

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(2-apy)]-BPh$_4$ (2b and 3b). Compound **1b** (200 mg, 0.37 mmol) was dissolved in 8 mL of CH_3OH, and $NaBPh_4$ (large excess) was added. 2-Acetylpyridine (58 mg, 0.48 mmol) was slowly added. Immediately a pale red solid precipitated. The solution was stirred for 30 min. The solid was filtered, washed with cold CH_3OH, and dried. The solid is a mixture of **2b** and **3b** in a

(10) Weissberger, A.; Proskauer, E. S. *Technique of Organic Chemistry*; Interscience: New York, 1955; Vol. VII.
(11) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

ratio 1:1 (yield 70%). Anal. Calcd (found) for $C_{40}H_{49}BRuO_3NP_2$: H, 6.28 (6.41); C, 62.83 (62.84); N, 1.83 (1.92). IR (CH_2Cl_2): ν_{CO} 1955 cm^{-1}; ν_{COMe} 1599 cm^{-1}. Complex **2b**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 10.11 (d, $^3J_{HH}$ = 4.2, H-6), 7.88 (m, H-5), 7.79 (t, $^3J_{HH}$ = 7.2, H-4), 7.70 (d, $^3J_{HH}$ = 7.9, H-3), 7.47 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7.3, *m*-H), 6.87 (t, $^3J_{HH}$ = 8.6 *p*-H), 2.56 (t, $^5J_{HH}$ = 3.8, COMe$_{lig}$), 2.52 (s, COMe), 1.00 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 7.2, PMe$_3$). ^{31}P{^{1}H} NMR: −3.6 (s, PMe$_3$). ^{13}C{^{1}H} NMR: 255.9 (br, *C*OMe), 206.5 (s, *C*OMe$_{lig}$), 204.7 (t, $^2J_{CP}$ = 14.3, CO), 164.7 (q, $^1J_{BC}$ = 49.2, C-*ipso*), 155.5 (s, C-2), 149.8 (s, C-6), 141.7 (s, C-5), 136.6 (s, *o*-C), 131.6 (s, C-4), 131.0 (s, C-3), 126.5 (s, *m*-C), 122.6 (s, *p*-C), 49.7 (s, CO*Me*), 27.1 (s, CO*Me*$_{lig}$), 14.2 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.8, PMe$_3$). Complex **3b**: ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 8.63 (d, $^3J_{HH}$ = 4.6, H-6), 7.63 (m, H-4), 7.59 (d, $^3J_{HH}$ = 7.6, H-3), 7.45 (t, $^3J_{HH}$ = 6.8, H-5), 7.47 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7.3, *m*-H), 6.87 (t, $^3J_{HH}$ = 8.6, *p*-H), 2.66 (t, $^5J_{HH}$ = 3.4, COMe$_{lig}$), 2.49 (s, COMe), 1.04 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 5.8, PMe$_3$). ^{31}P{^{1}H} NMR: −2.8 (s, PMe$_3$). ^{13}C{^{1}H} NMR: 256.5 (br, *C*OMe), 208.0 (s, *C*OMe$_{lig}$), 204.7 (t, $^2J_{CP}$ = 14.3, CO), 165.8 (s, C-2), 164.7 (q, $^1J_{BC}$ = 49.2, C-*ipso*), 153.6 (s, C-6), 141.3 (s, C-4), 136.6 (s, *o*-C), 132.2 (s, C-3), 131.7 (s, C-5), 126.5 (s, *m*-C), 122.6 (s, *p*-C), 45.4 (s, CO*Me*), 27.1 (s, CO*Me*$_{lig}$), 14.3 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.9, PMe$_3$).

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(2-bzpy)]BPh$_4$ (4b). The procedure was the same as that for **2b** and **3b** (yield 68%). IR (CH_2Cl_2): ν_{CO} 1956 cm^{-1}; ν_{COMe} 1610 cm^{-1}. ^{1}H NMR (in CD_2Cl_2, 294 K, *J* values in Hz): δ 10.23 (d, $^3J_{HH}$ = 5.5, H-6), 8.18 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.1, H-3), 7.83 (t, $^3J_{HH}$ = 7.0, H-4), 7.82 (dd $^3J_{HH}$ = 5.3, $^4J_{HH}$ = 1.7, H-5), 7.81 (d, $^3J_{HH}$ = 7.2, H-4′), 7.68 (d, $^3J_{HH}$ = 7.0, H-2′), 7.64 (t, $^3J_{HH}$ = 7.3, H-3′), 7.31 (m, *o*-H), 6.99 (t, $^3J_{HH}$ = 7.4, *m*-H), 6.85 (t, $^3J_{HH}$ = 7.2, *p*-H), 2.57 (s, COMe), 1.05 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 7.2, PMe$_3$). ^{31}P{^{1}H} NMR: 17.4 (s, PMe$_3$). ^{13}C{^{1}H} NMR: 255.5 (t, $^2J_{CP}$ = 9.2, *C*OMe), 204.6 (t, $^2J_{CP}$ = 14.7, CO), 201.2 (s, *C*OPh), 164.4 (q, $^1J_{BC}$ = 49.2, C-*ipso*), 156.6 (s, C-2), 156.1 (s, C-6), 149.3 (s, C-3), 140.8 (br, C-1′), 136.3 (s, *o*-C), 134.7 (s, C-4), 133.3 (s, C-5), 131.2 (s, C-4′), 130.1 (s, C-2′ and C-3′), 126.1 (s, *m*-C), 122.2 (s, *p*-C), 49.4 (s, CO*Me*), 13.9 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 28.9 PMe$_3$).

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(2,2′-dpk)]BPh$_4$ (6b). The procedure was the same of **2b** and **3b** (yield 66%). IR (CH_2Cl_2): ν_{CO} 1956 cm^{-1}; ν_{COMe} 1607 cm^{-1}. ^{1}H NMR (in CD_2Cl_2, 298 K, *J* values in Hz): δ 10.23 (dd, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 1.1, H-6), 9.67 (dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.7, H-6′), 8.79 (d, $^3J_{HH}$ = 5.8, H-3′), 8.16 (d, $^3J_{HH}$ = 6.9, H-3), 8.02 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.7, H-5′), 7.96 (t, $^3J_{HH}$ = 5.12, H-4), 7.89 (m, H-5), 7.65 (m, H-4′), 7.30 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 6.9, *m*-H), 7.87 (t, $^3J_{HH}$ = 6.6, *p*-H), 2.59 (s, COMe), 1.05 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 3.7, PMe$_3$). ^{31}P{^{1}H} NMR: −3.3 (s, PMe$_3$). ^{13}C{^{1}H} NMR: 255.7 (s, *C*OMe), 205.1 (s, CO), 196.6 (s, *C*O of the ligand), 164.8 (q, $^1J_{BC}$ = 49.6, C-*ipso*), 155.7 (s, C-6), 152.5 (s, C-2), 150.3 (s, C-6′), 149.8 (s, C-2′), 140.7 (s, C-3′), 139.1 (s, C-3), 136.6 (s, *o*-C), 136.4 (s, C-5′), 131.5 (s, C-4), 129.9 (s, C-5), 128.0 (s, C-4′), 126.4 (s, *m*-C), 122.5 (s, *p*-C), 49.8 (s, CO*Me*), 14.3 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.8, PMe$_3$)

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement coefficients (Table S1), anisotropic displacement coefficients (Table S2), H-atom coordinates and isotropic displacement coefficients (Table S3), and bond lengths and bond angles (Table S4) for **4b** (8 pages). Ordering information is given on any current masthead page.

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