5048 *Inorg. Chem.* **2009,** *48,* 5048–5048
DOI:10.1021/ic900661z

Inorganic Chemistry
Additions and Corrections

Anthony P. Shaw, Bradford L. Ryland, Jack R. Norton,* Daniela Buccella, and Alberto Moscatelli: Electron Exchange Involving a Sulfur-Stabilized Ruthenium Radical Cation

Page 5806. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data in the section describing the preparation of $RuCl_2(PPh_3)_3$ are incorrect. The material prepared by this method contained some residual PPh_3 (which did not adversely affect its use as a starting material). The ^{31}P NMR resonance that we reported was actually that of free PPh_3. The ^{31}P NMR resonance of the complex is a broad singlet at δ 41.7 and is not easily detected in dilute solutions. The broadness is attributed to fluxional behavior. Washing our crude material with Et_2O several more times and drying under vacuum overnight gave a sample with a satisfactory microanalysis. However, the $^{31}P\{^1H\}$ NMR spectrum of this sample still showed a small amount of free PPh_3, presumably due to a dissociation equilibrium. In 1966, Stephenson and Wilkinson noted that solutions of $RuCl_2(PPh_3)_3$ in acetone or benzene were nonconducting but molecular weight determinations (by membrane osmometry) gave low values; these observations were attributed to the facile dissociation of PPh_3.[1] The correct NMR and analytical data for our pure sample of $RuCl_2(PPh_3)_3$ follow. The amount of free PPh_3 (due to the dissociation equilibrium) was small and did not appear in our $^{13}C\{^1H\}$ NMR spectrum. The ^{13}C NMR resonances were referenced to $CDCl_3$ (δ 77.16). The ^{31}P NMR resonances were referenced to 85% H_3PO_4 (δ 0.0) contained in a sealed capillary inside the NMR tube. $^{13}C\{^1H\}$ NMR (concentrated solution, 75 MHz, $CDCl_3$): δ 127.5 (br, s), 129.4 (s), 144.0 (m), 135.4 (br, s). $^{31}P\{^1H\}$ NMR (concentrated solution, 121.5 MHz, $CDCl_3$): δ −4.7 (free PPh_3, s), 41.7 (the complex, br s). Anal. Calcd for $C_{54}H_{45}Cl_2P_3Ru$: C, 67.64; H, 4.73; Cl, 7.40. Found: C, 67.43; H, 4.70; Cl, 7.44. We thank Michael Silver of Hope College for bringing this to our attention.

Pages 5810−5812. We have since performed additional experiments that support our hypotheses in eqs 10−12 and Scheme 3. A solution analogous to that in eq 10 was prepared in CD_2Cl_2. When this solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy, temperature-dependent line broadening like that in Figure 8 was observed over a range of −56.0 to +7.4 °C. This result confirms that $[CpRu(dppe)CD_3CN][BPh_4]$ and free thiol (generated from **1** in CD_3CN but not in CD_2Cl_2) are not required in the processes that broaden the peaks of **1** and **3** in Figure 8. Another issue pertinent to eqs 10−12 is whether the amine used to generate the **1**/**3** mixture, NEt_3, is serving as a one-electron reductant.[2−4] To test this possibility, a saturated CD_3CN solution of **3** was treated with a small substoichiometric amount of $Fc[PF_6]$ (ferrocenium hexafluorophosphate), thereby generating a trace of **5**. The resulting **3**/**5** electron exchange substantially broadened the ^1H NMR peaks of **3**. When excess NEt_3 (with respect to the initial **3**) was added, the spectrum remained unchanged because NEt_3 did not reduce **5**. *Therefore, NEt_3 does not participate in electron-transfer processes relevant to eqs 10−12 or Scheme 3*. When the same control test was performed with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), the trace of **5** was reduced and the resulting spectrum of **3** was sharp. In eq 9, where a *single equivalent* of DBN was used to deprotonate **1**, the resulting spectra of **3** were broad. In this case, the low concentration of DBN was not sufficient to reduce the trace of **5** responsible for **3**/**5** exchange. The above observations provide further support for our original hypotheses (eqs 10−12 and Scheme 3) as an explanation for the temperature-dependent line broadening observed in **1**/**3** mixtures (Figure 8).

Page 5812. The spectra in Figure 9 were obtained from a CD_2Cl_2 solution.

---

[1] Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945–956.

[2] Adenier, A.; Chehimi, M. M.; Gallardo, I.; Pinson, J.; Vilà, N. *Langmuir* **2004**, *20*, 8243–8253.

[3] Jonsson, M.; Wayner, D. D. M.; Lusztyk, J. *J. Phys. Chem.* **1996**, *100*, 17539–17543.

[4] Eastland, G. W.; Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1551–1557.