$T_{1\,\mathrm{min}}$ value is equal to 171 ms. The difference (1.3 s^{-1}) between the calculated rate and the observed one is probably due to a contribution to the relaxation of hydride ligands from the phosphine protons and the deuterons of the solvent molecules.[3,7] For example, in the complex $Re_2H_4(\mu\text{-}H)_4(PMe_3)_4$, there are few phosphine protons and the averaged $T_{1\,\mathrm{min}}$ of H ligands is 162 ms.[17]

Thus, a MHDD interaction can significantly decrease ^{1}H T_1 relaxation times. For this reason one should be very careful with quantitative interpretation of the T_1 data in the case of hydride complexes of V, Mn, Co, Nb, and Re.[19a]

Note Added in Proof. An analysis of the factors contributing to the spin–lattice relaxation time T_1 for $OsH_4(P(Tol)_3)_3$ and related hydrides, including, among other things, the large metal–hydride dipole–dipole interaction contributing to a short $T_{1\,\mathrm{min}}$ in $Re_2H_8(PEt_2Ph)_4$, appeared after this work was entered into production (see: Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184).

---

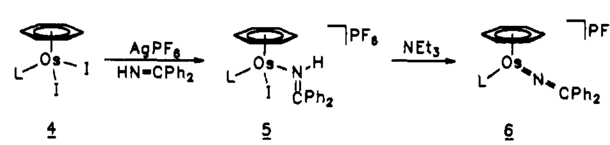
(19) (a) Note: After submission of our manuscript we become aware[19b] of an independent paper (Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. Submitted for publication in *Magn. Reson. Chem.*) where a very similar conclusion has been formulated. (b) Crabtree, R. H. Private communication.

Institute of Organo-Element Compounds
Academy of Sciences of the USSR
117813 Moscow, USSR

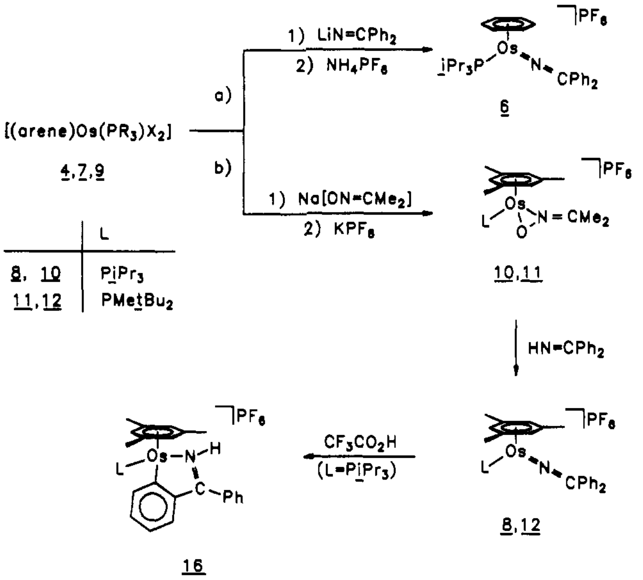
Dmitry G. Gusev
Alexey B. Vymenits
Vladimir I. Bakhmutov*

Received February 28, 1991

Scheme I. L = P-i-Pr3



Scheme II



New Synthetic Routes to Azavinylidene Half-Sandwich Type Complexes

Among transition-metal complexes containing metal–nitrogen double bonds, nitrene–metal as well as azavinylidene–metal compounds have received increasing attention.[1,2] In connection with our studies on vinylidene–metal derivatives of the general type [(ring)M(=C=CRR′)(L)],[3,4] we recently found that the corresponding *azavinylidene* complexes $[(C_6H_6)Os({=}N{=}CRR')P(Me)(t\text{-}Bu)_2]PF_6$ (**3**) are accessible from $[(C_6H_6)OsH(I)P(Me)(t\text{-}Bu)_2]$ (**1**), $AgPF_6$, and ketoximes in good yields.[5] In two cases, the cationic hydrido oxime derivatives $\{(C_6H_6)OsH[N(OH){=}CRR']P(Me)(t\text{-}Bu)_2\}PF_6$ (**2**) have been characterized as intermediates which by elimination of water give the final products.

During attempts to prepare analogues of **3** with ligands L other than $P(Me)(t\text{-}Bu)_2$, we observed that the type of phosphine ligand used plays a critical role in the course of the reaction. Replacement of $P(Me)(t\text{-}Bu)_2$ even by P-*i*-Pr$_3$ causes difficulties that were unexpected owing to the similar size of the two phosphine molecules.[6]

In trying to escape the dilemma, we discovered that ketimines are more suitable starting materials for the synthesis of azavinylidene–osmium complexes [(arene)Os(=N=CRR′)(L)]X than ketoximes. Here we describe three alternative pathways to prepare compounds of the above-mentioned type and in addition report the synthesis of the first azavinylidene–*iridium* complex containing $[(C_5Me_5)IrP(Me)(t\text{-}Bu)_2]$ as a structural unit.

Under conditions similar to those used for the preparation of **3**, compound **4**[7] reacts with $HN{=}CPh_2$ in presence of $AgPF_6$ to give the orange-yellow imine complex **5** (see Scheme I).[8] If after filtration the reaction mixture is treated with NEt_3, orange crystals of the azavinylidene complex **6** are isolated in 78% yield.[9] A similar procedure has also been applied for the preparation of the corresponding mesitylene–osmium derivative $[(mes)Os({=}N{=}CPh_2)(P\text{-}i\text{-}Pr_3)]PF_6$ (**8**),[9] in this case using $[(mes)Os(P\text{-}i\text{-}Pr_3)Cl_2]$

---

(1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) Recent publications on azavinylidene–metal complexes: (a) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68. (b) Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343. (c) Erker, G.; Frömberg, W.; Krüger, C.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400. (d) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (e) Green, M.; Mercer, R. J.; Morton, C. E.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 422. (f) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377. (g) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (h) Barron, A. R.; Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2947. (i) Dormond, A.; Aaliti, A.; Elbouadili, A.; Moise, C. *J. Organomet. Chem.* **1987**, *329*, 187. (j) Woo, H.-G.; Tilley, T. D. *J. Organomet. Chem.* **1990**, *393*, C6. (k) Feng, S. G.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6477. (l) Merzweiler, K.; Fenske, D.; Hartmann, E.; Dehnicke, K. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1989**, *44B*, 1003. (m) Klinzing, P.; El-Kholi, A.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1989**, *569*, 83.

(3) M = Rh; ring = C_5H_5; L = P*i*Pr$_3$: (a) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414. (b) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397. (c) Werner, H.; Brekau, U. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1989**, *44B*, 1438.

(4) M = Os; ring = C_6H_6; L = P*i*Pr$_3$, P(Me)(*t*-Bu)$_2$: (a) Weinand, R.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1145. (b) Knaup, W. Ph.D. Thesis, Universität Würzburg, 1988. (c) Werner, H.; Weinand, R.; Knaup, W.; Peters, K.; von Schnering, H.-G. Manuscript in preparation.

(5) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 248.

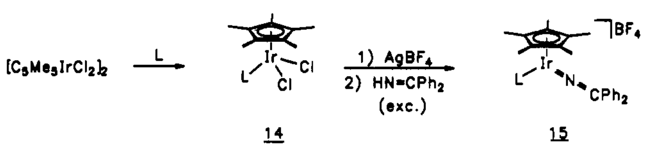
(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(7) Werner, H.; Kletzin, H.; Roder, K. *J. Organomet. Chem.* **1988**, *355*, 401.

(8) Selected IR and NMR spectroscopic data of **5** are as follows. IR (KBr): ν(NH) 3235 cm^{-1}. ^{1}H NMR (60 MHz, CD_3NO_2): δ 10.93 (s, br, 1 H, NH), 7.6 (m, 10 H, C_6H_5), 5.77 (s, 6 H, C_6H_6), 2.90 (m, 3 H, PC*H*CH$_3$), 1.33 (dd, 18 H, *J*(PH) = 13.7 Hz *J*(HH) = 7.1 Hz, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −1.74 (s, P-*i*-Pr$_3$), −145.48 (sept, *J*(PF) = 707.4 Hz, PF$_6$).

0020-1669/91/1330-3118$02.50/0

Scheme III. L = PMe-*t*-Bu$_2$



(**7**) (mes = 1,3,5-trimethylbenzene)[10] as the starting material. The structure proposed for **6** and **8** is supported by elemental analysis, by conductivity measurements, and in particular by comparison of the spectroscopic data[9] with those of [(C$_6$H$_6$)Os(=N=CPh$_2$)P(Me)(*t*-Bu)$_2$]PF$_6$. This complex was characterized by a single-crystal X-ray analysis.[5]

To avoid using AgPF$_6$ (which is not only expensive but often contains impurities of HF), we have also developed routes to prepare **6**, **8**, and the P(Me)(*t*-Bu)$_2$ analogue **12** from LiN=CPh$_2$ or directly from the imine HN=CPh$_2$ (see Scheme II). According to route a, the diiodo compound **4** reacts with LiN=CPh$_2$ in toluene/ether to give primarily the iodide of the cationic azavinylidene–osmium complex, which is then transformed into the more stable PF$_6$ salt **6** by treatment with NH$_4$PF$_6$. In route b, the starting material **7** or {(mes)Os[P(Me)(*t*-Bu)$_2$]Cl$_2$} (**9**)[10] is first treated with Na[ON=CMe$_2$] in the presence of KPF$_6$ to afford the oximato compounds **10** or **11**,[11] which on further reaction with HN=CPh$_2$ in dichloromethane give the final products **8** and **12**.[12] The corresponding azavinylidene derivative {(mes)Os[=N=C(Et)(Ph)]P(Me)(*t*-Bu)$_2$}PF$_6$ (**13**) containing one ethyl and one phenyl group at the β-C atom is prepared analogously, using **11** as starting material.[12] The yield of **8**, **12**, and **13** according to route b is almost quantitative. The formation of free oxime HON=CMe$_2$ in the reaction of **11** with HN=CPh$_2$ has been proved by NMR measurements.

With regard to the spectroscopic data of **13**,[12] we note that in the ^{1}H NMR spectrum two signals for the PC(CH$_3$) methyl protons are observed, indicating that the *t*-Bu groups are diastereotopic. The conclusion is that the plane of the C$_\beta$, C$_{ipso}$ and CH$_2$ carbon atoms of the azavinylidene ligand is perpendicular to the plane formed by the phosphorus, the osmium atom, and the midpoint of the mesitylene ring. The proposed "allene-like" structure is also supported by the appearance of two signals for the CH$_2$ protons of the C-bound ethyl group, which give rise to an AB pattern in the ^{1}H NMR spectrum.[12]

The "imine route" has also been the key to success in preparing the azavinylidene iridium complex [(C$_5$Me$_5$)Ir(=N=CPh$_2$)P(Me)(*t*-Bu)$_2$]BF$_4$ (**15**) (Scheme III). The synthesis of the starting material {(C$_5$Me$_5$)Ir[P(Me)(*t*-Bu)$_2$]Cl$_2$} (**14**) is straightforward (yield 94%) following the procedure described by Maitlis et al. for [(C$_5$Me$_5$)Ir(PPh$_3$)Cl$_2$].[13] Treatment of **14** with an equimolar amount of AgBF$_4$ in acetone at −30 °C initially gives a green solution (presumely containing the dinuclear cation {(C$_5$Me$_5$)$_2$Ir$_2$[P(Me)(*t*-Bu)$_2$]$_2$(μ-Cl)$_2$}$^{2+}$), which upon addition of excess HN=CPh$_2$ affords **15**.[14] This compound can also be prepared from **14**, LiN=CPh$_2$, and NH$_4$PF$_6$, but in low yield. The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data[14] leave no doubt that the iridium complex **15** is related in structure to the osmium analogue **12**.

We are presently trying (1) to prepare other types of azavinylidene complexes of the platinum group metals and (2) to study the reactivity of the metallacumulene systems. As one of the preliminary results it should be mentioned that treatment of **8** with trifluoracetic acid gives the orthometalated complex **16** (Scheme II) in quantitative yield.[15] We note that recently

---

(9) Synthesis of **6** and **8** is as follows. A solution of HN=CPh$_2$ (70 μL, 0.39 mmol) in CH$_2$Cl$_2$ (5 mL) was added at −78 °C to a solid mixture of **4** or **7** (0.19 mmol) and AgPF$_6$ (48 mg, 0.19 mmol). After being warmed to room temperature and stirred for 20 min, the suspension was filtered and NEt$_3$ (50 μL, 0.36 mmol) was added to the filtrate. The mixture was stirred for 15 min, and the solvent was removed. The residue was dissolved in CH$_2$Cl$_2$ (1 mL) and the solution chromatographed on Al$_2$O$_3$ (neutral, activity grade III). With CH$_2$Cl$_2$, a red fraction was collected, which was brought to dryness in vacuo. The residue was recrystallized from CH$_2$Cl$_2$/OEt$_2$ to give orange crystals in 78% (**6**) and 47% (**8**) yield: mp 169 °C dec (**6**), 174 °C dec (**8**); equiv conductivity Λ = 77 (**6**), 81 (**8**) cm^2 Ω^{-1} cm^{-1}. Spectroscopic data for **6** are as follows. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 7.6 (m, 10 H, C$_6$H$_5$), 6.37 (s, 6 H, C$_6$H$_6$), 2.37 (m, 3 H, PC*H*CH$_3$), 1.12 (dd, 18 H, *J*(PH) = 14.7 Hz, *J*(HH) = 7.1 Hz, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 29.93 (s, P-*i*-Pr$_3$), −145.55 (sept, *J*(PF) = 706.8 Hz, PF$_6$). ^{13}C NMR (50.2 MHz, CD$_3$NO$_2$): δ 159.0 (d, *J*(PC) = 4.4 Hz, =*C*Ph$_2$), 81.28 (s, C$_6$H$_6$), 27.29 (d, *J*(PC) = 29.4 Hz, P*C*HCH$_3$), 20.12 (s, PCH*C*H$_3$), signals for C$_6$H$_5$ carbons not mentioned. Spectroscopic data for **8** are as follows. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 7.45 (m, 10 H, C$_6$H$_5$), 6.15 (s, 3 H, C$_6$*H*$_3$Me$_3$), 2.57 (s, 9 H, C$_6$H$_3$*Me*$_3$), 2.23 (m, 3 H, PC*H*CH$_3$), 1.10 (dd, 18 H, *J*(PH) = 14.3 Hz, *J*(HH) = 6.9 Hz, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 28.23 (s, P-*i*-Pr$_3$), −145.48 (sept, *J*(PF) = 707.2 Hz, PF$_6$). ^{13}C NMR (22.5 MHz, CD$_3$NO$_2$): δ 158.92 (s, =*C*Ph$_2$), 96.62 (d, *J*(PC) = 2.6 Hz, *C*$_{ring}$–CH$_3$), 82.20 (d, *J*(PC) = 2.6 Hz, *C*$_{ring}$–H), 27.51 (d, *J*(PC) = 28.2 Hz, P*C*HCH$_3$, 20.89 (s, C$_{ring}$–*C*H$_3$), 20.05 (s, PCH*C*H$_3$), signals for C$_6$H$_5$ carbons not mentioned.

(10) Werner, H.; Stahl, S.; Kohlmann, W. *J. Organomet. Chem.* **1991**, *409*, 285.

(11) Synthesis of **10** and **11** is as follows. A solution of **7** (124 mg, 0.23 mmol) or **9** (118 mg, 0.22 mmol) in CH$_3$OH (10 mL) was treated at room temperature with KPF$_6$ (50 mg, 0.315 mmol) and Na[ON=CMe$_2$] (30 mg, 0.315 mmol). After the mixture was stirred for 30 min, the solvent was removed and the residue was extracted with CH$_2$Cl$_2$ (10 mL). The extract was brought to dryness in vacuo, and the crude product was recrystallized from CH$_2$Cl$_2$/OEt$_2$ to give yellow-brown crystals in 88% (**10**) and 86% (**11**) yield: mp 140 °C dec (**10**), 135 °C dec (**11**); equiv conductivity Λ = 76 (**10**), 78 (**11**) cm^2 Ω^{-1} cm^{-1}. Spectroscopic data for **10** are as follows. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 5.80 (s, 3 H, C$_6$*H*$_3$Me$_3$), 2.45 (s, 9 H, C$_6$H$_3$*Me*$_3$), 2.28 (m, 3 H, PC*H*CH$_3$), 2.13 (s, 3 H, NCCH$_3$), 2.03 (s, 3 H, NCCH$_3$), 1.22 (dd, 18 H, *J*(PH) = 13.9 Hz, *J*(HH) = 6.9 Hz, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 20.03 (s, P-*i*-Pr$_3$), −145.53 (sept, *J*(PF) = 707.1 Hz, PF$_6$). Spectroscopic data for **11** are as follows. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 5.98 (s, 3 H, C$_6$*H*$_3$Me$_3$), 2.38 (s, 9 H, C$_6$H$_3$*Me*$_3$), 2.23 (s, 3 H, NCCH$_3$), 2.18 (s, 3 H, NCCH$_3$), 1.78 (d, 3 H, *J*(PH) = 8.3 Hz, PCH$_3$), 1.24 (d, 9 H, *J*(PH) = 13.7 Hz, PCCH$_3$), 1.19 (d, 9 H, *J*(PH) = 13.7 Hz, PCCH$_3$).

(12) Synthesis of **12** and **13** is as follows. A solution of **11** (145 mg, 0.21 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with an excess (ca. 0.6 mmol) of HN=C(R)Ph (R = Ph, Et). After being stirred for 30 min at room temperature, the solution was concentrated to ca. 1 mL and treated with ether (10 mL) to give a red-brown microcrystalline precipitate. The mother liquor was removed and the solid repeatedly washed with pentane and dried in vacuo: yield 87% (**12**) and 82% (**13**); mp 187 °C dec (**12**), 184 °C dec (**13**); equiv conductivity Λ = 67 (**12**), 74 (**13**) cm^2 Ω^{-1} cm^{-1}. Complex **8** can be prepared analogously, starting with **10** and a 4-fold excess of HN=CPh$_2$ to give **8** in 95% yield. Spectroscopic data for **12** are as follows. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.5 (m, 10 H, C$_6$H$_5$), 6.28 (s, 3 H, C$_6$*H*$_3$Me$_3$), 2.51 (s, 9 H, C$_6$H$_3$*Me*$_3$), 1.95 (d, 3 H, *J*(PH) = 8.7 Hz, PCH$_3$), 1.09 (d, 18 H, *J*(PH) = 14.3 Hz, PCCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 19.99 (s, PMe-*t*-Bu$_2$), −145.13 (sept, *J*(PF) = 707.1 Hz, PF$_6$). Spectroscopic data for **13** are as follows. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.4 (m, 5 H, C$_6$H$_5$), 6.24 (s, 3 H, C$_6$*H*$_3$Me$_3$), 3.50 (ddq, 1 H, *J*(HH) = 14.8 and 7.4 Hz, *J*(PH) = 1.4 Hz, one H of C*H*$_2$CH$_3$), 3.41 (ddq, 1 H, *J*(HH) = 14.8 and 7.4, *J*(PH) = 1.4 Hz, one H of C*H*$_2$CH$_3$), 2.50 (s, 9 H, C$_6$H$_3$*Me*$_3$), 1.96 (d, 3 H, *J*(PH) = 8.5 Hz, PCH$_3$), 1.23 (d, 9 H, *J*(PH) = 14.2 Hz, PCCH$_3$), 1.19 (t, 3 H, *J*(HH) = 7.4 Hz, CH$_2$C*H*$_3$), 0.99 (d, 9 H, *J*(PH) = 14.2 Hz, PCCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 18.05 (s, PMe-*t*-Bu$_2$), −145.26 (sept, *J*(PF) = 706.9 Hz, PF$_6$).

(13) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(14) Synthesis of **15** is as follows. A solution of **14** (41 mg, 0.07 mmol) in acetone (10 mL) was treated at −30 °C with a solution of AgBF$_4$ (14 mg, 0.07 mmol) in acetone (5 mL). A white solid precipitated. After addition of HN=CPh$_2$ (60 μL, 0.3 mmol), a color change of the solution from green to red occurred. The reaction mixture was filtered, the filtrate was brought to dryness in vacuo, and the residue recrystallized from CH$_2$Cl$_2$/OEt$_2$ to give a red-violet crystalline solid in 61% yield: mp 166 °C dec; equiv conductivity Λ = 76 cm^2 Ω^{-1} cm^{-1}. ^{1}H NMR (60 MHz, CDCl$_3$): δ 7.3 (m, 10 H, C$_6$H$_5$), 1.81 (d, 15 H, *J*(PH) = 1.5 Hz, C$_5$Me$_5$), 1.67 (d, 3 H, *J*(PH) = 8.8 Hz, PCH$_3$), 0.89 (d, 18 H, *J*(PH) = 14.4 Hz, PCCH$_3$). ^{31}P NMR (36.2 MHz, CDCl$_3$): δ 25.28 (s, PMe-*t*-Bu$_2$), −145.26 (sept, *J*(PF) = 706.9 Hz, PF$_6$). ^{13}C NMR (50.2 MHz, CD$_2$Cl$_2$): δ 161.8 (br, =*C*Ph$_2$), 96.26 (s, *C*$_5$Me$_5$), 37.17 (d, *J*(PC) = 23.7 Hz, P*C*CH$_3$), 29.31 (d, *J*(PC) = 3.6 Hz, PC*C*H$_3$), 10.48 (s, C$_5$(*C*H$_3$)$_5$), 7.35 (d, *J*(PC) = 33.7 Hz, PCH$_3$), signals for C$_6$H$_5$ carbons not mentioned.

Boncella et al.[16] have described a similar arene–*ruthenium* derivative (containing a phenyl group on the nitrogen and a hydrogen on the β-C atom) that was obtained from [(C_6Me_6)Ru(PMe_3)Cl_2], 2 equiv of benzylideneaniline, and 2 equiv of $AgBF_4$. We suppose that the driving force for the formation of **16** (which is an isomer of **8**) is the prefered attack of electrophiles at the N (and not the β-C) atom of the M=N=C unit, which would be in accord with the behavior of vinylidene–rhodium complexes toward electrophilic reagents.[17]

Acknowledgment. We are grateful for support provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and thank the DEGUSSA AG for generous gifts of chemicals.

Supplementary Material Available: A list summarizing the results of CHN analysis for complexes **5**, **6**, **8**, **10–13**, **15**, and **16** (1 page). Ordering information is given on any current masthead page.

---

(15) Synthesis of **16** is as follows. A solution of **8** (108 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was treated with CF_3CO_2H (11 μL, 0.14 mmol) and stirred for 1 h at room temperature. The solution was concentrated to ca. 1 mL and chromatographed on Al_2O_3 (neutral, activity grade V) with CH_2Cl_2. After removal of the solvent, the residue was recrystallized from CH_2Cl_2/pentane to give orange crystals in 97% yield: mp 216 °C dec; equiv conductivity $\Lambda = 72\ cm^2\ \Omega^{-1}\ cm^{-1}$. IR (KBr): ν(NH) 3325 cm^{-1}. ^1H NMR (90 MHz, CD_3NO_2): δ 9.58 (s, br, 1 H, NH), 8.31–7.06 (m, br, 9 H, C_6H_4 and C_6H_5), 5.62 (s, 3 H, $C_6\mathit{H}_3Me_3$), 2.31 (s, 9 H, $C_6H_3\mathit{Me}_3$), 2.24 (m, 3 H, $PC\mathit{H}CH_3$), 1.17 (dd, 9 H, J(PH) = 14.5 Hz, J(HH) = 7.3 Hz, $PCHC\mathit{H}_3$), 0.94 (dd, 9 H, J(PH) = 13.1, J(HH) = 7.1 Hz, $PCHC\mathit{H}_3$). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 0.96 (s, P-*i*-Pr_3), −145.57 (sept, J(PF) = 707.1 Hz, PF_6). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 191.72 (d, J(PC) = 1.5 Hz, N=*C*), 174.62 (d, J(PC) = 11.7 Hz, Os—*C*), 101.44 (d, J(PC) = 2.2 Hz, C_{ring}—CH_3), 82.10 (d, J(PC) = 2.2 Hz, C_{ring}—H), 25.36 (d, J(PC) = 27.1 Hz, $P\mathit{C}HCH_3$), 21.15 (s, $PCH\mathit{C}H_3$), 19.43 (s, $PCH\mathit{C}H_3$), 18.59 (d, J(PC) = 2.2 Hz, C_{ring}—$\mathit{C}H_3$), other signals for C_6H_5 and C_6H_4 carbons not mentioned.

(16) Martin, G. C.; Boncella, J. M. *Organometallics* **1989**, *8*, 2968.

(17) Wolf, J.; Werner, H. *J. Organomet. Chem.* **1987**, *336*, 413.

Institut für Anorganische Chemie
Universität Würzburg
Am Hubland
D-8700 Würzburg, Germany

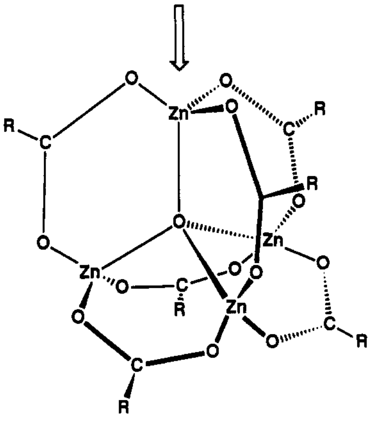
Thomas Daniel
Michael Müller
Helmut Werner*

Received January 29, 1991

Transition-Metal Clusters as Substituents. Synthesis, Structure, and Thermal Decomposition of $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$

The synthesis of high-nuclearity main-group–transition-element clusters in soluble molecular forms is well illustrated by recent research in the metal chalcogenide area.[1-3] The various approaches have included the use of zeolites[4] and inverse micelles[5] to induce or guide the organization. We have previously demonstrated physical association of the tailed clusters $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_xOH)$ (x = 4, 5) in solution and in the solid state.[6] This spontaneous association of metal clusters is also of interest in terms of developing molecular assemblies for conversion into designed materials. In the case of pyrolytic conversion of an assembled precursor, the binding forces must be much stronger than the physical ones responsible for the association of $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_xOH)$. Indeed the binding energies must approach those that hold the unwanted ligands on the metal atoms. Hence, we have begun to explore cluster association determined by the covalent bonding of a set of suitably modified clusters to an atom center or centers.[7] One possibility is classical coordination of clusters containing a suitable ligand functional group to an oxidized metal center. The work of Seyferth and co-workers provides one compound with the desired characteristics, i.e., $(CO)_9Co_3(\mu_3\text{-}CCOOH)$.[8]

Zinc(II) forms a bis(acetato) complex, but of more interest, it also forms a tetranuclear acetate with a centered oxygen atom, i.e., $Zn_4O(MeCOO)_6$.[9] In this compound the six acetates edge-bridge a zinc tetrahedron with an oxygen atom in the center (structure **1**).[10] Hence, all four zinc atoms are tetrahedrally coordinated to four oxygen atoms leading to an environment similar to that found in the lattice of bulk zinc oxide. Indeed, the emission properties of this acetate derivative have been used to demonstrate that it behaves as if it were the smallest zinc oxide particle.[11] For these reasons we set out to investigate the coordination of $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ to zinc.



1

In the event, the reaction of $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ with $ZnEt_2$ cleanly produces a single deep purple-brown product, which precipitates in Et_2O. The solution infrared spectrum of the product suggests chelation via the carboxylate anion functionality,[12] and the shift in the CO stretches of the $Co_3(CO)_9$ fragments to higher frequency indicates coordination to a positive center.[13] Further, the analysis of the crystalline material is consistent with the formulation $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$ (I).[14] The overall isolated yield of this product (1-g scale) based on the cobalt cluster is 60%. The molecular weight of I is 3186.2, and the solubility of the compound in THF is impressive considering it is more than 40% by weight metal.

Crystals suitable for diffraction were grown by Et_2O diffusion into a THF solution of I, and definitive structural characterization followed crystallographic analysis via X-ray diffraction techniques.[15] The structure, shown in Figure 1, is basically that of

---

(1) Fenske, D.; Hollnagel, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1390.

(2) Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6856.

(3) You, J.-F.; Snyder, B. S.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1067.

(4) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *247*, 669.

(5) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327.

(6) Basil, J. D.; Aradi, A. A.; Bhattacharyya, N. K.; Rath, N. P.; Eigenbrot, C.; Fehlner, T. P. *Inorg. Chem.* **1990**, *29*, 1260.

(7) Related approaches have been described. Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1990**, *112*, 8552. Johnson, B. F. G.; Lewis, J.; Massey, A. D.; Raithby, P. R.; Wong, W. T. *J. Organomet. Chem.* **1990**, *397*, C28. Davis, S. J.; Howard, J. A. K.; Musgrove, R. J.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 624. Jaeger, J. T.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1746.

(8) Hallgren, J. E.; Eschbach, C. S.; Seyferth, D. *J. Am. Chem. Soc.* **1972**, *94*, 2547.

(9) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983.

(10) Koyama, H.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 112.

(11) Kunkely, H.; Vogler, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1204.

(12) Grigor'ev, A. I. *Russ. J. Inorg. Chem.* **1963**, *8*, 409.

(13) IR (THF, cm^{-1}): 2109 w, 2070 s, 2042 vs (all CO); 1557 w, 1386 m, 1351 vw (all COO^-).

(14) Anal. Calcd for $Zn_4Co_{18}C_{66}O_{67}$: Zn, 8.20; Co, 33.31; C, 24.87; O, 33.62. Found (dried under vacuum): Zn, 7.68; Co, 30.52; C, 24.77; O, 33.41.

0020-1669/91/1330-3120$02.50/0