Journal of Organometallic Chemistry, 101 (1975) C43—C44

Preliminary communication

ELECTROCHEMICAL OXIDATION OF π-$C_5H_5M(CO)_3$ (M = Mn, Re) AND THEIR DERIVATIVES

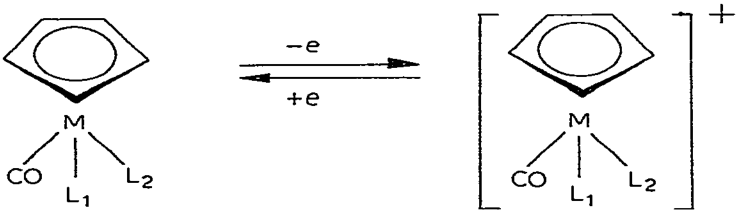
L.I. DENISOVICH, N.V. ZAKURIN, S.P. GUBIN* and A.G. GINZBURG
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

(Received September 30th, 1975)

Summary

It was found that cyclopentadienyltricarbonyl-manganese and -rhenium and their derivatives oxidize at the platinum microelectrode via one monoelectron step. The half wave potentials of the investigated compounds depend upon the ligand environment of the manganese and rhenium atoms.

Unlike ferrocene and dibenzene chromium sandwich complexes the electrochemical oxidation of the aromatic metal carbonyl complexes of the type π-$C_5H_5M(CO)_3$ (M = Mn, Re) has not yet been investigated. We found that cyclopentadienyltricarbonyl-manganese and -rhenium (CTM, CTR) and their derivatives may oxidize at the platinum microelectrode in 0.1 *N* Et_4NBF_4 in CH_3CN via one monoelectron step. For most compounds the oxidation is electrochemically reversible. The product of one-electron oxidation was a 17 electronic cation whose stability could widely vary with the structure of the complex.



M = Mn, Re, X = H, $COCH_3$, Alk etc.
L = CO, L = PR_3 (R = Ar, Alk), $C_6H_5C{=}CC_6H_5$
L_1L_2 = $P(C_6H_5)_2(CH_2)_nP(C_6H_5)_2$, n = 2,3

Unlike ferrocene ($E_{1/2}$ = + 0.01 V) under the same conditions the oxidation of CTM is more difficult*. CTR and its derivatives oxidize at more positive potentials ($E_{1/2}$(CTR) = +1.22 V) than the respective CTM derivatives.

---

*The potentials were measured with respect to 0.01 *M* $Ag/AgClO_4$ in 0.1 *N* $EtNBF_4$ in CH_3CN.

The effect of substituents in the π-C_5H_5 ring of the compounds investigated on the redox potentials is similar to that of ferrocene [1], dibenzenechromium [2] and arenecyclopentadienyliron cations [3] where the metal electrons are known to participate in redox reactions.

The half-wave potentials depend heavily upon the ligand environment of the manganese and rhenium atoms. Replacement of one CO group by the stronger σ-donor ligand PPh_3 shifts $E_{1/2}$ to less positive values (e.g. $E_{1/2}$ = +0.25 V, when $L_1 = CO$, $L_2 = P(C_6H_5)_3$, M = Mn)*. However, an essential shift of $E_{1/2}$ was observed upon introduction of two triphenylphosphine groups or chelating diphosphinic ligands $PR_2(CH_2)_nPR_2$. In this case the degenerated cation may undergo further oxidation. The polarogram shows the second wave at the more positive potentials ($E_{1/2}(1) = -0.50$ V, $E_{1/2}(2) = +0.79$ V for π-$C_5H_5MnCOPPh_2(CH_2)_2PPh_2$).

It should be noted that the CTM derivatives investigated oxidize somewhat more easily than the previously described one-electron oxidation of the cationic π-cyclopentadienylnitrosylmanganese complexes $[\pi\text{-}C_5H_5Mn(NO)LL']^+$ (where L and L′ are Lewis bases) [5] and carbenic complexes π-$C_5H_5Mn(CO)_2CXY$ [6].

References

1 S.P. Gubin and E.G. Perevalova, Dokl. Akad. Nauk SSSR, 143 (1962) 1351.
2 I.A. Suskina, B.G. Gribov, E.A. Idrisova, L.I. Denisovich and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 425.
3 A.N. Nesmeyanov, L.I. Denisovich, S.P. Gubin, N.A. Vol'kenau, E.I. Sirotkina and I.N. Bolesova, J. Organometal. Chem., 20 (1969) 169.
4 P.M. Treichel, K.P. Wagner and H.J. Much, J. Organometal. Chem., 86 (1975) C13.
5 P. Hydes, J.A. McCleverty and G. Orchard, J. Chem. Soc. (A), (1971) 3660.
6 J.A. McCleverty, D.G. Orchard, J.A. Connor, E.M. Jones, J.P. Lloyd and P.D. Rose, J. Organometal. Chem., 30 (1971) C75.

---

*While this paper was in preparation the electrochemical oxidation of π-$C_5H_5Mn(CO)_2PPh_3$, π-$C_5H_5MnCO(PPh_3)_2$ and π-C_5H_5MnCO(diphos) was reported [6].