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COMMUNICATION

AMIDINATO COMPLEXES OF THE PLATINUM METALS AND AN AVID CARBONYL ABSTRACTION REACTION

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Abstract—Platinum metal hydrido and trifluoroacetato complexes react with N,N′-diphenylamidines, PhN═C(R)—NHPh (R = H, Me, Et, Ph), giving the amidinato derivatives $Ru\{PhNC(R)NPh\}_2(CO)(PPh_3)$, $MX\{PhNC(R)NPh\}(CO)(PPh_3)_2$ and $IrX_2\{PhNC(R)NPh\}(PPh_3)_2$ (M = Ru, Os; X = H, Cl; $X_2 = H_2$, Cl_2 or HCl). The reactions of $RuH_2(PPh_3)_4$ and $OsH_4(PPh_3)_3$ with amidines are accompanied by an avid alcohol decarbonylation reaction to form the carbonyls $MH\{PhNC(R)NPh\}(CO)(PPh_3)_2$.

N,N′-Diarylamidinate anions, $ArNC(R)NAr^-$ (R = H, alkyl or aryl), have recently attracted much attention as bridging ligands in binuclear complexes of the general form $M_2\{ArNC(R)NAr\}_4$.[1–4] However, the ability of these anions to function as chelating ligands is no less interesting in view of the strained nature of the resulting four-membered metallocycles.[5–7] We now report that N,N′-diphenylamidines PhNC(R)NHPh (R = H, Me, Et or Ph) react with platinum metal hydrides and trifluoroacetates according to the general equations of (1) and (2), respectively, to afford an extensive series of chelate amidinato complexes.

$$L_nM{-}H + PhNC(R)NHPh \longrightarrow L_{n-1}M\{PhNC(R)NPh\} + H_2 \quad (1)$$

$$L_nM{-}O_2CCF_3 + PhNC(R)NHPh \longrightarrow L_{n-1}M\{PhNC(R)NPh\} + CF_3CO_2H \quad (2)$$

These reactions provide the most prolific series of amidinato complexes reported to date giving a very valuable route to this class of compounds. They also furnish many new examples of the relatively rare cleavage of N—H bonds by platinum metal species,[8,9] and in the case of certain ruthenium complexes are accompanied by a particularly avid carbonyl abstraction reaction.

Ruthenium and osmium hydrides, $MHCl(CO)(PPh_3)_3$ and $RuH_2(CO)(PPh_3)_3$, react with N,N′-diphenylamidines, PhNC(R)NHPh (R = H, Me, Et, or Ph), in toluene over a period of 4 to 7 h to afford the products $MCl\{PhNC(R)NPh\}(CO)(PPh_3)_2$ and $RuH\{PhNC(R)NPh\}(CO)(PPh_3)_2$, respectively. The osmium precursor $OsH_2(CO)(PPh_3)_3$ undergoes similar reactions under more forcing conditions (2-methoxyethanol, 24 h) to afford the products $OsH\{PhNC(R)NPh\}(CO)(PPh_3)_2$. The iridium hydrides *mer*-$IrH_3(PPh_3)_3$ and $IrHCl_2(PPh_3)_3$ also react with amidines in boiling toluene to afford the products $IrH_2\{PhNC(R)NPh\}(PPh_3)_2$ and $IrCl_2\{PhNC(Ph)NPh\}(PPh_3)_2$, respectively. In the presence of added base (NEt_3) the latter reaction performed in refluxing benzene affords the hydridic species $IrHCl\{PhNC(R)NPh\}(PPh_3)_2$.

The ruthenium and osmium trifluoroacetates $M(O_2CCF_3)_2(CO)(PPh_3)_2{\cdot}MeOH$ react with N,N′-diphenylamidines under mild conditions (benzene; Ru 1/2 h, Os, 2 h) to yield the monosubstituted products $M(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2$ and under more forcing conditions (boiling toluene 3–24 h) to afford $MH\{PhNC(R)NPh\}(CO)(PPh_3)_2$ (M = Ru, R = H; M = Os, R = H, Me, Et or Ph) or $M\{PhNC(R)NPh\}_2(CO)(PPh_3)$ (M = Ru, R = Me, Et, Ph). The new chelate amidinato complexes are obtained in good yield as air-stable yellow crystalline solids and have been fully characterized by elemental analysis and spectroscopic methods.

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Syntheses of amidinato complexes from carbonyl free ruthenium and osmium precursors are accompanied by an efficient alcohol decarbonylation process. Thus, the hydrides $RuH_2(PPh_3)_4$ and $OsH_4(PPh_3)_3$ react with amidines under reflux in toluene containing small amounts of ethanol to give the carbonylated products $MH\{PhNC(R)NPh\}(CO)(PPh_3)_2$. This behaviour of amidines is in marked contrast to that found for carboxylic acids (RCO_2H) and 1,3-diphenyltriazene (PhNNNHPh) which react with $RuH_2(PPh_3)_4$ in neat refluxing 2-methoxy ethanol to afford $RuH(O_2CR)(PPh_3)_3$[10] and $Ru(PhNNNPh)_2(PPh_3)_2$,[11] respectively, with no evidence of carbonyl abstraction from the solvent in either case. We suggest that reactions involving all three ligands pursue a common initial step to generate intermediates of the general form $RuH(chelate)(PPh_3)_3$. Subsequent reactions then depend upon the properties of the individual ligands and can be tentatively rationalized as follows. The carboxylates $RuH(O_2CR)(PPh_3)_3$ fail to react further because the relatively high acidity of the carboxylic acids and the relatively poor coordinating power of the carboxylate anions militate against carbonyl abstraction and bis(chelate) formation, respectively. The 1,3-diaryltriazenes because of their relatively low basicity and good chelating characteristics form bis(chelates). However, the closely related amidines are sufficiently basic to generate the alkoxide anions necessary for carbonylation to occur.

REFERENCES

1. J. C. Le, M. Y. Chavan, L. J. Chau, J. L. Bear and K. M. Kadish, *J. Am. Chem. Soc.* 1985, **107**, 7195.
2. P. Piraino, G. Bruno, S. Lo Schiavo, F. Laschi and P. Zanello, *Inorg. Chem.* 1987, **26**, 2205.
3. F. A. Cotton and R. Poli, *Polyhedron* 1987, **6**, 1625.
4. F. A. Cotton, M. Matusz and R. Poli, *Inorg. Chem.* 1987, **26**, 1472.
5. L. D. Brown, S. D. Robinson, A. Sahajpal and J. A. Ibers, *Inorg. Chem.* 1977, **16**, 2728.
6. B. Gaylani, M. Kilner, C. I. French, A. J. Pick and S. C. Wallwork, *Acta Cryst.* 1991, **C47**, 257.
7. F. A. Cotton and R. Poli, *Inorg. Chim. Acta* 1988, **141**, 91.
8. D. R. Schaad and C. R. Landis, *J. Am. Chem. Soc.* 1990, **112**, 1628 and refs therein.
9. F. T. Lapido and J. S. Merola, *Inorg. Chem.* 1990, **29**, 4172.
10. S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.* 1973, 1912.
11. K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.* 1974, 1205.